SEDIMENTS OF SAGINAW BAY, LAKE HURON:

ELEMENTAL COMPOSITION AND ACCUMULATION RATES

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ABSTRACT

During the period from 1975 through 1978, sediment cores and grab samples were obtained from over 100 sites in lower Saginaw Bay. Selected samples were analyzed for grain size, organic and inorganic carbon, over 30 elements and both cesium-137 and lead-210. The study has revealed an extensive mud deposit in the lower bay covering about 400 km^2 oriented approximately with bathymetric contours. The clay content of this deposit exceeds 50% toward the center with the mean grain size increasing toward deposit margins. Calcium family elements (Ca, Mg, and inorganic carbon) are preferentially concentrated at the southwestern end of the deposit either because of the distribution of source materials or because of prevailing currents in the system. In contrast, iron and organic carbon exhibit highest concentrations in sediments with highest content of clay-size particles. Most other elements, including contaminant metals (Cr, Cu, Ni, Pb, Zn) have surface concentrations which correlate strongly with concentrations of iron and organic carbon ($r \geq 0.9$; N = 30).

Vertical distributions of radionuclides and contaminant metals reveal a zone of constant activity (or concentration) which extends from the sediment-water interface to depths ranging from 10 to 25 cm. This zone of uniform composition varies systematically within the deposit, tending to be greatest toward the center, and is probably the result of extensive mixing by zoobenthos (predominantly oligochaetes). About 90% of the zoobenthos occur within the zone of mixing determined radiometrically. Benthos densities range from 10,000 to 50,000 per m^2 and are sufficient to completely mix sediments annually.

Because of extensive mixing, sedimentation rates may not be reliably determined from profiles of Cs-137 in this system. However, lead-210 dating appears valid and yields sedimentation rates ranging from about 0.07 to 0.24 $g/cm^2/yr$ (0.1-0.6 cm/yr). Highest rates occur toward the southwestern end of the deposit and decrease with increasing distance from the mouth of the Saginaw River. Radiometric mixed depths, in combination with sedimentation rate values, provide estimates of particle residence times in the mixed layer ranging from 11 to 60 years and averaging 30 years. Contaminant metal deposition rates as of 1975 are estimated using a model of steady-state mixing and exponential loading with a 20-year doubling time in combination with sedimentation rate data.

Annual loadings are estimated (in metric tons/year) as: Cr, 54; Cu, 28; Ni, 30; P, 420; Pb, 40; and Zn, 86.

Surface concentrations of contaminant metals (and most other elements) are consistently lower in the bay mud deposits than in open lake deposits. Intense local sources do not lead to higher concentrations within the deposit mainly because of extensive downward reworking of surface materials, and to a lesser degree, because of dilution by inert allochthonous materials. When corrected for "dilution" effects, concentration of chromium are considerably higher in the bay muds. Relative to underlying sediments, the contaminant metals are highly enriched in surface materials and mean vertically integrated amounts (exceeding background) levels ($\mu g/cm^2$) are: Cr, 280; Cu, 160; Ni, 160; Pb, 230; and Zn, 490). These values far exceed the excess element accumulation in deposits of the open lake. Thus, while surface concentrations of contaminant elements, with the exception of chromium, are not particularly distinctive, the vertically integrated amounts are strikingly high

illustrate the effectiveness of vertical reworking processes in diluting contaminants reaching the mud. The total amount of cesium-137 stored in the deposits is about 64 Ci compared with an estimated 158 Ci deposited over the same area from cumulative atmospheric fallout. As tributary contributions may be ignored (but possibly not exchange from the open lake) the muds are no more than 40% efficient in retention of the radionuclide. Total inventories of metal contaminants in the lower bay (metric tons) are: Cr, 1,000; Cu, 590; Ni, 590; P, 11,000; Pb, 850; and Zn, 1,800.

Fluxes of nutrients from cores collected during the period from April through November 1978 were determined from changes in concentrations in water overlying sediments incubated at prevailing in situ temperatures. Mean values for the period were: P, -530 $\mu g/cm^2/yr$; $N(NH_3)$, $+200$ $\mu g/cm^2/yr$; $N(NO_3)$, -360 $\mu g/cm^2/yr$; and Si, 3,000 $\mu g/cm^2/yr$. Releases of Si constitute a major input of Si into the Bay. The flux of silicon from sediments exhibits an annual cycle ranging from about 1,500 $\mu g/cm^2/yr$ in the spring to a maximum of about 6,000 $\mu g/cm^2/yr$ in August. The mean flux may be reliably predicted from thermodynamic expressions and the sediment temperature. During the fall months the flux (at constant temperature) is strongly correlated with the numbers of chironomid larvae present. Correlations between other nutrient fluxes and organism densities are generally insignificant. The mean flux of silicon based on pore water concentration gradients and estimates of the effective molecular diffusion coefficient were only about 660 μg $Si/cm^2/yr$. Significantly higher direct fluxes suggest that Si release from sediments is not diffusion-limited but dependent on the rate at which materials dissolve at the sediment-water interface.

CONTENTS

INTRODUCTION

This is the second of three reports dealing with the composition of recent sediments of Lake Huron and the rate of accumulation of metal contaminants. The aims of the report include: (1) determination of recent sedimentation rates both by radiometric methods and other means, (2) identification of elemental contaminants by examination of concentration profiles in dated sediment cores, (3) development of contour maps for sections of the lake which show the concentration of metal contaminants and their present and historical rates of accumulation, (4) estimation of the total amount of various contaminants stored in sediments, (5) identification of the origins of metal contaminants in selected cores, and (6) recognition and quantitative treatment of processes affecting sedimentary records of radioactivity and metal contaminants and the exchange of substances between sediments and overlying water. The results of the research reported in this Lake Huron sediment series represent a natural extension of the work of Thomas et al. (1973), who provided the first extensive and systematic mapping of the surficial sediments of Lake Huron, and that of Kemp and Thomas (1976), who provided the first limited exploratory study of the distribution of metal contaminants in pollen-dated cores from this Lake.

The reports in the series deal with southern Lake Huron (Robbins 1980), Saginaw Bay and northern Lake Huron. Areas of the lake treated in each report are indicated in Figure 1. This report, focusing on Saginaw Bay, emphasizes the lower part of the bay as can be seen from the distribution of coring locations shown in Figure 2. The 1973 study of Thomas et al. indicated that sediments of the outer bay were comprised of sand and therefore relatively
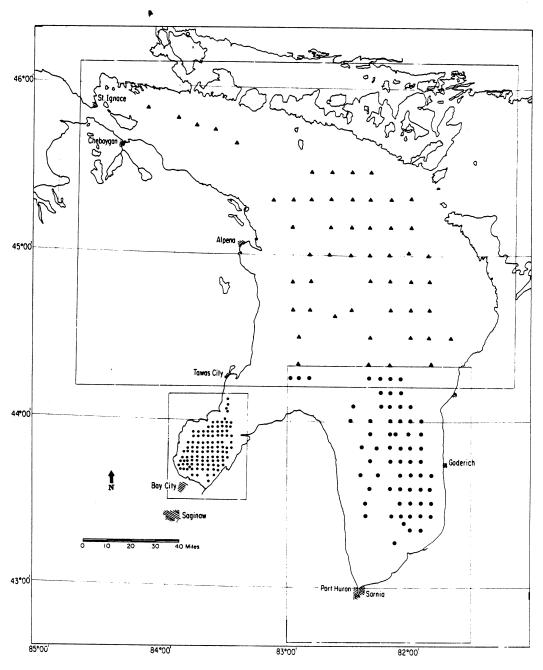
Figure 1. Sediment coring locations in Lake Huron. Sampling was conducted throughout the entire lake from 1974 through 1978.
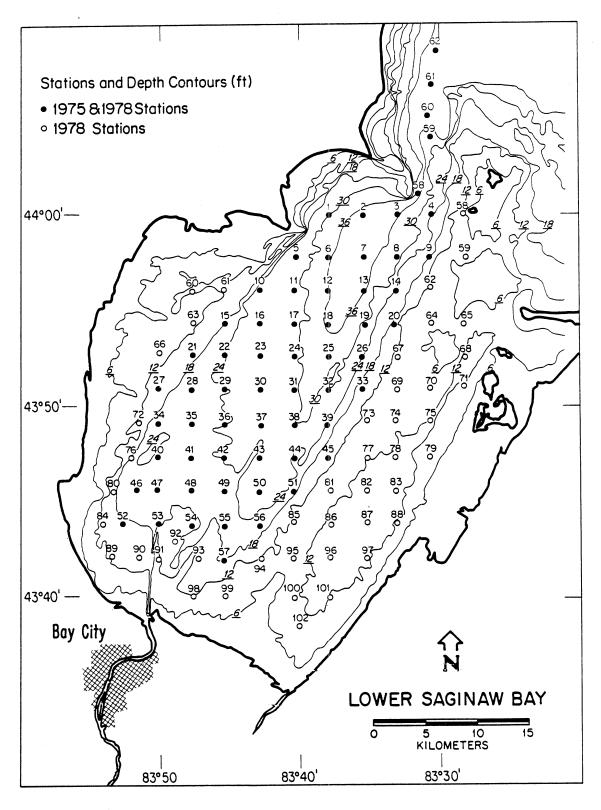
Figure 2. Sediment sampling sites in Saginaw Bay.

uninteresting from the standpoint of significant accumulations of contaminants. Although the Thomas et al. study did not include the lower bay, the earlier work of Wood (1964) showed that the lower part of the bay possessed an area of fine-grained sediments of considerable extent.

As the fine-grained sediments are the primary carriers of contaminants, this area is a probable receptor of contamination issuing from the Saginaw River. In this report, the results of analyses of many samples from the several hundred cores collected in the lower bay are summarized.

METHODS

FIELD METHODS

Sediment samples were collected at 57 stations in Saginaw Bay during April and August of 1975. The locations of the 1975 stations, shown in Figure 2, cover in considerable detail most of the corable areas in the lower bay. In 1978 the entire lower bay was resampled at over 100 stations. Cores were collected wherever possible and supplemented by Ponar grab samples of uncorable sediments (sand and gravel). The additional 1978 sampling sites are shown in Figure 2 as open circles. Sediment cores were collected with a 3-inch diameter gravity core (Benthos, Inc., Falmouth, Mass.). Cores contained within plastic liners were hydraulically extruded and sectioned aboard ship. Details of the sediment collection and processing methods are provided in the Southern Lake Huron Report (Robbins 1980).

In addition, for this report, a series of cores were taken for nutrient flux measurements. Cores collected by the above methods were extruded into short plastic liners approximately 25 cm long. Care was taken to preserve approximately 10 cm of overlying water and to disturb the core minimally

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during the transfer process. The short sections of core with overlying water were placed in a water-bath incubator, the temperature of which was adjusted to match the _in situ_ sediment temperature. The overlying water in the cores was continuously aerated and mixed by introduction of filtered air from a 3/8" section of Tygon tubing extending a few cm into the water overlying each core. A maximum of 21 cores could be incubated simultaneously. During the period from April to November 1978, selected sites in the lower bay were revisited eight times to collect cores for nutrient flux determinations. Fluxes were inferred from measurement of the concentration of nutrients in overlying water as a function of time. Approximately every 24 hours for one week, 20 mL of water was withdrawn from each core (about 5-7% of the total volume of overlying water), filtered immediately through a phosphate-free pre-rinsed 0.45 micron (Millipore®) filter, and frozen for subsequent analysis. During the course of the flux study, over 40 cores were examined.

LABORATORY METHODS

The methods for determination of certain sediment characteristics and composition of sediments are described in considerable detail in the Southern Lake Huron Report (Robbins 1980). Methods are described for determination of bulk density, fraction dry weight, zoobenthos composition, activity of cesium-137, total and inorganic carbon, elements via Atomic Absorption Spectrophotometry (AAS) on acid-peroxide extracts, lead-210, amorphous silicon, and elements in whole sediment as determined via Neutron Activation Analysis (NAA). Concentrations of nutrients in pore water and, in the flux experiments, in overlying water are determined by conventional colorimetric methods as described by Strickland and Parsons (1972).

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In addition, for this report, grain-size distributions have been measured

by conventional methods, employing sieving for peroxide-cleaned sediments with

mean grain diameters exceeding 63 μm and pipette analysis of the sieved

materials with mean grain sizes less than 63 μm. Details of these methods are

described by Royse (1970).

RESULTS AND DISCUSSION

PHYSICAL CHARACTERISTICS OF SEDIMENTS

The distribution of grain size in surface sediments of the lower bay is

summarized in Figures 3-5 in terms of the major size categories: clay, silt,

and sand. In analyzing over 150 sediment cores, the 1-2-cm interval was

chosen on the assumption that it provides a better representation of the

distribution of grain sizes of quasi-permanent surface deposits than does the

0-1 cm interval. This uppermost layer (0-1 cm) consists of a fluid, highly

mobile flocculent phase overlying all corable sediments in the bay. The lim-

ited comparisons possible from the vertical dependence of grain size

distributions in cores suggest that there is generally little difference in

grain size distribution between the 0-1 and 1-2 cm intervals of sediment.

Inspection of Figures 3-5 shows that the lower bay possesses an extensive

area of mud (clay plus silt) which generally lies within the deeper waters and

covers roughly one quarter of the area of the lower bay. Areas outside the

mud deposit are generally comprised of sand with isolated areas of gravel and

coarser materials. Even within the mud deposit, surface sediments generally

have detectable amounts of fine sand. Only six samples out of 102 contained

no measurable amounts of sand. The mean grain size of surface sediments in

the lower bay is shown in Figure 6. Note that accumulation of finer materials
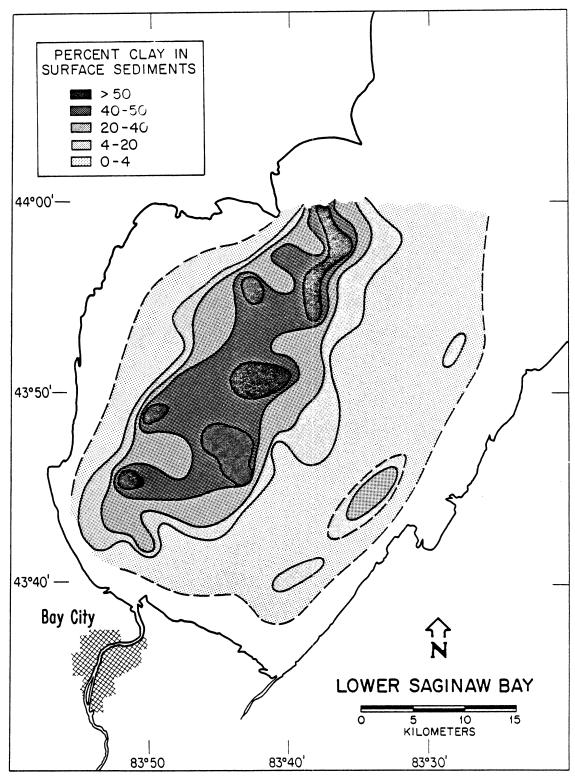
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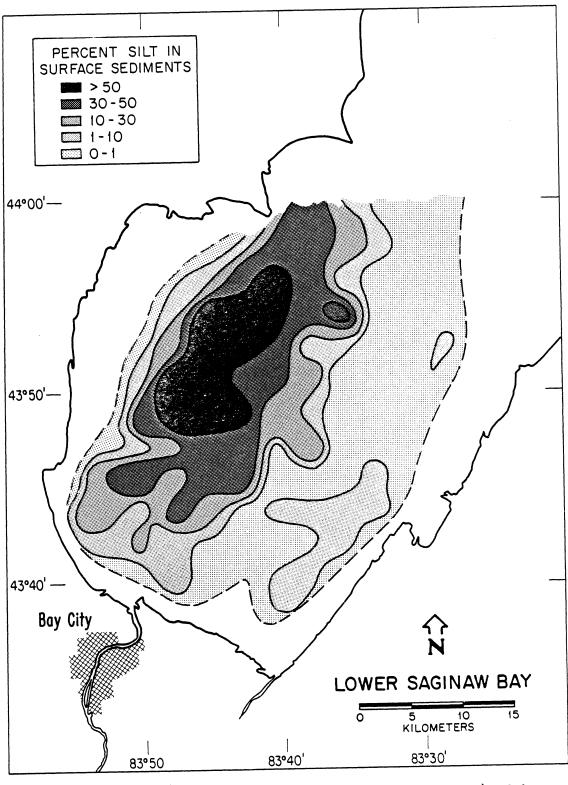Figure 3. Percent clay in surface sediments (1-2 cm depth) of lower Saginaw Bay.

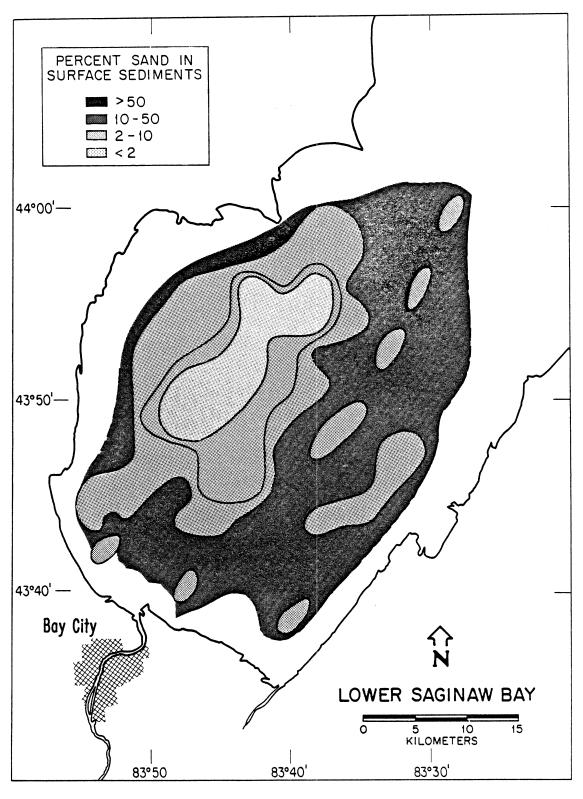Figure 4. Percent silt in surface sediments (1-2 cm depth) of lower Saginaw Bay.

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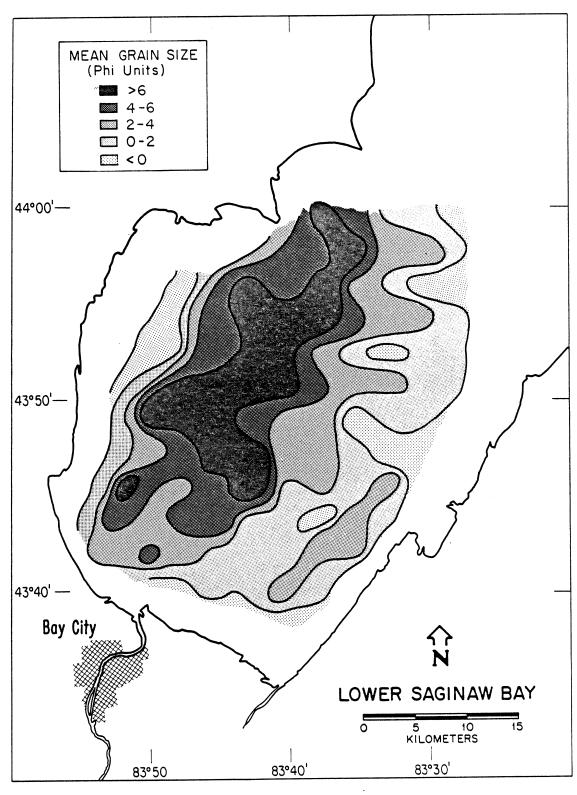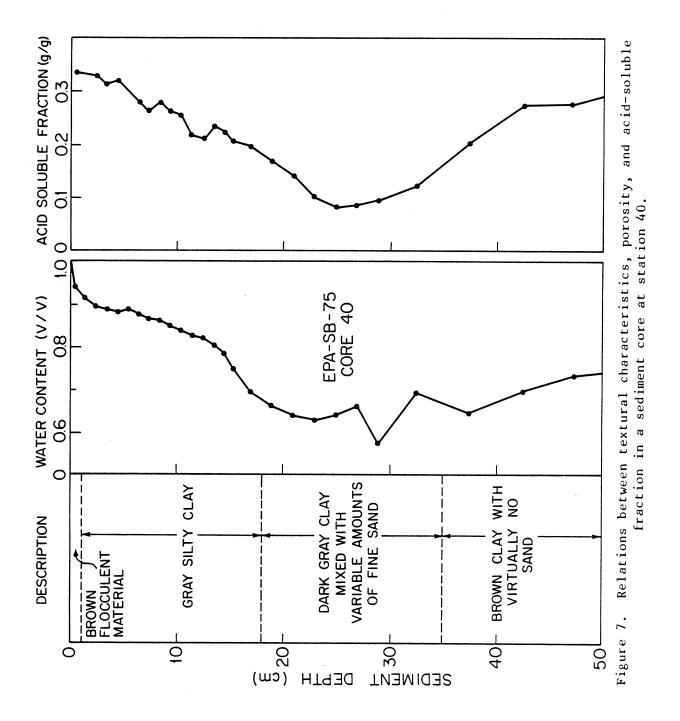Figure 5. Percent sand in surface sediments (1-2 cm depth) of lower Saginaw Bay.

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Figure 6. Mean grain size (phi units) of surface sediments of lower
Saginaw Bay.

(phi 2) occurs to a limited extent in the southeastern region of the bay in locally deep water (cf. Fig. 2 for bathymetric data).
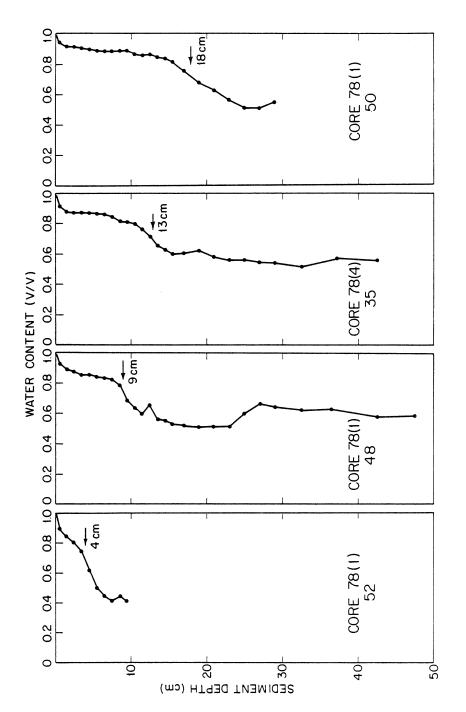
The fractional water content by volume (porosity) of surface sediments (1-2 cm) shows minor but systematic variations over the mud deposit. Highest porosities tend to occur toward the center of the deposit and decrease toward the margins where a greater proportion of sand occurs. No water content measurements were made outside the mud deposits, as only grab samples could be obtained for which water content as well as depth determinations are inaccurate. The vertical distribution of water content in cores shows systematic variations which are important for interpretation of radioactivity and metal profiles. An example is provided in Figure 7 (Core: EPA-SB-75-40). A qualitative description of sediment textural characteristics is shown as a function of sediment depth along with the porosity and the fraction of dry sediment by weight which is soluble on treatment with acid and concentrated hydrogen peroxide. Both the porosity and the soluble fraction decrease with increasing sediment depth down to about 20 cm, remain constant more or less between 20 and 35 cm, and then rise slightly below 35 cm to at least 50 cm. The principal reason for this systematic decrease in porosity over the upper 20 cm is variable dilution of fine grained sediments by sand. Sediments between 20 and 35 cm contain considerable sand (~50%). Below the layer of sandy clay-silt is a layer, starting at about 35 cm in the core (Fig. 7), of virtually sand-free clay. It is important to note that although compaction can account for some of the decrease in water content near the sediment surface, its role is comparatively minor below depths of a few cm, as can be seen by comparison of the water content and acid soluble fraction in Figure 7. This core typifies the vertical structure of the mud deposits in the lower

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ACID SOLUBLE FRACTION (g/g)

0   0.1   0.2   0.3

WATER CONTENT (V/V)

0   0.6   0.8   1.0

EPA-SB-75
CORE 40

DESCRIPTION

BROWN FLOCCULENT MATERIAL

GRAY SILTY CLAY

DARK GRAY CLAY MIXED WITH VARIABLE AMOUNTS OF FINE SAND

BROWN CLAY WITH VIRTUALLY NO SAND

SEDIMENT DEPTH (cm)

0   10   20   30   40   50

Figure 7. Relations between textural characteristics, porosity, and acid-soluble fraction in a sediment core at station 40.
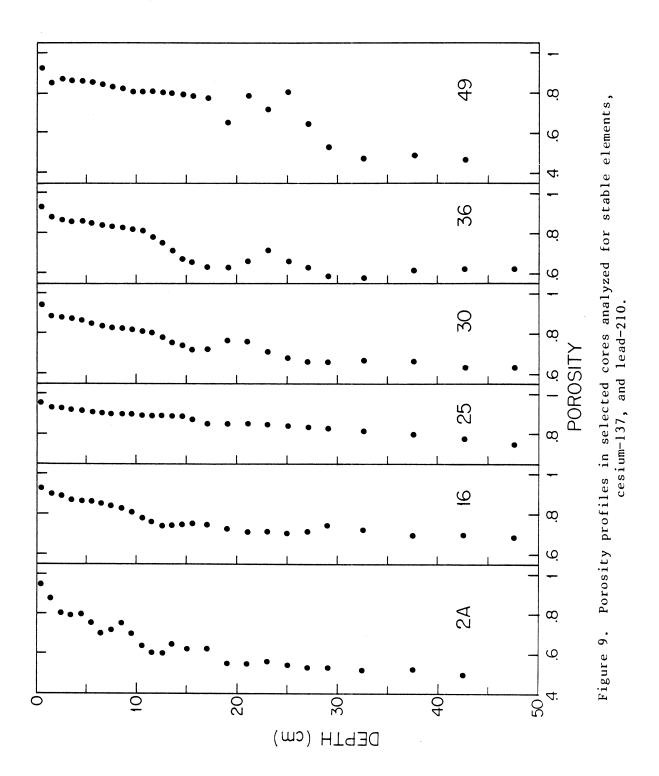
bay: zone 1 (fluid flocculent sediment) is roughly 1 cm thick, overlaying

zone 2, gray silty clay with a sand content which gradually increases with

sediment depth, followed by zone 3, which is a region of silty clay with a

relatively uniform and high amount of fine sand, underlain by a clay (zone 4)

of higher water content (greasy) of indeterminate thickness. The thickness of

the zones varies systematically with location within the mud deposit.

The depth of the transition between zone 2 (mud with sand content increasing

with depth) and zone 3 (clay-silt with uniformly high amounts of fine sands)

occurs roughly where the porosity, ϕ, is 0.7 and the rate of change of

porosity, $\frac{d\phi}{dz}$, with depth is greatest (i.e., $\frac{1}{\phi}\frac{d\phi}{dz}$). In the case of Core 78-40

(Fig. 7), this depth is about 15 cm. Porosity profiles for several other

cores are shown in Figures 8 and 9. Porosity transition depths (mud layer

thickness) vary from 4 to 18 cm in the examples. The porosity of surface

sediments is shown in Figure 10. The systematic variation in the mud

thickness is illustrated in Figure 11. Thickest deposits occur toward the

center of the depositional area and the thickness is correlated with the

fraction of the sediment which is clay.

COMPOSITION OF SURFACE SEDIMENTS

The pH of surface sediments measured in April is shown in Figure 12.

Values tend to be highest (exceeding pH 8.00) toward the margins of the mud

deposit. Lowest pH values tend to be centrally located within the deposit and

are as low as about 7.2 pH units. The platinum electrode potential (Eh) shown

in Figure 13 also tends to be highest toward the deposit perimeter with values

exceeding 400 mv. Within the deposit the electrode potential is less than 100

mv over roughly half the area. These trends toward lower pH and Eh values

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Figure 8. Porosity profiles (water content) in selected cores. Arrows indicate location of Me transition region.

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Figure 9. Porosity profiles in selected cores analyzed for stable elements, cesium-137, and lead-210.

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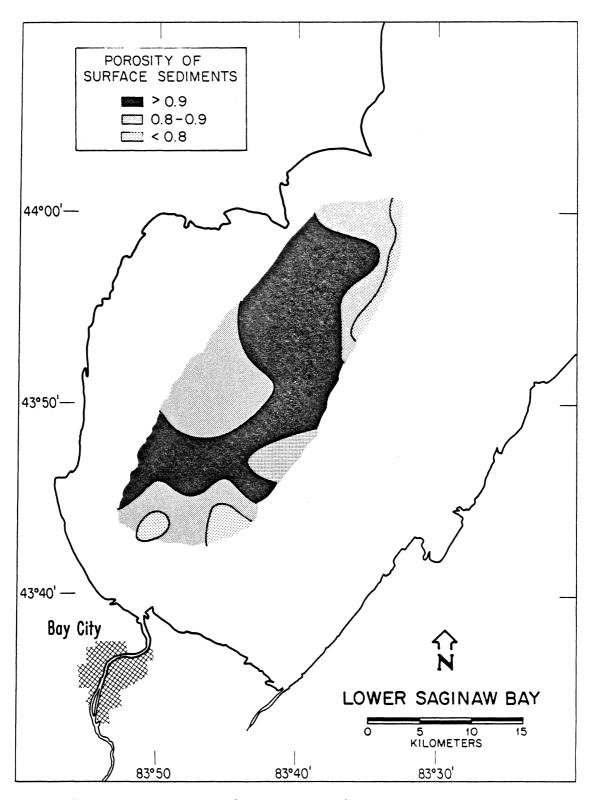
Figure 10. Porosity (water content) of surface sediments.

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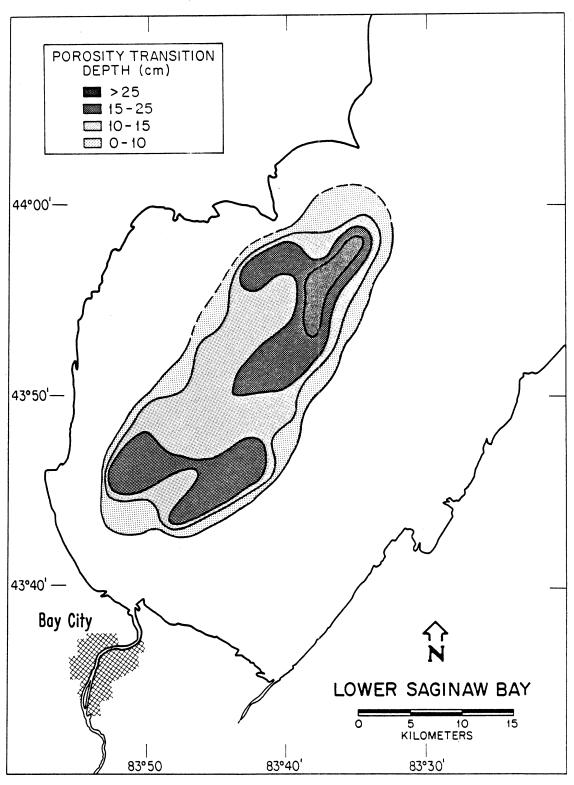
Figure 11. Depth of maximum fractional porosity change (see text).

pH of Surficial Sediments
April 1975

44°00'

7.52   7.64   8.16   7.95

7.57   7.44   7.35   7.51   7.49

7.40   7.37   748   7.45   7.73

7.34   7.25   7.50   7.41   7.48   7.75
7.50

7.96   7.28   7.36   7.64   743   7.51

7.40

7.21   7.48   7.36   7.30   7.74

43°50'

7.47   7.60   7.47   7.47   7.52   7.45

7.51   7.48   7.49   7.58   7.39   7.81

7.50   7.40

7.67   7.51   7.39   7.55   7.36   7.58
7.50

7.58   7.59   7.81   7.35   800

7.60

7.58

43°40'

BAY CITY

LOWER SAGINAW BAY

MILES
0 1 2 3 4 5 6 7 8 9
N

83°50'   83°40'   83°30'
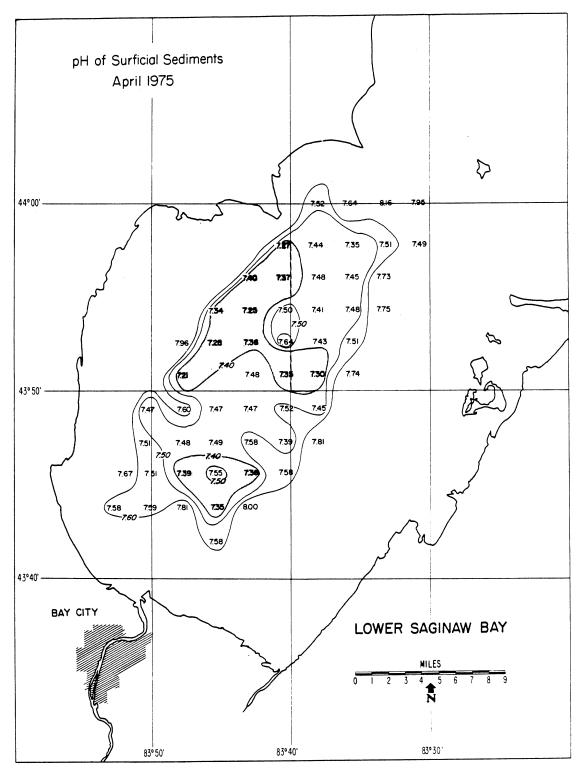
Figure 12.   pH of surface sediments (April 1975).

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Electrode Potential (Eh, mv.)
of Surficial Sediments
April 1975

44°00'

172 ▲   108 ▲   490 ■   460 ■

110

172 ▲   121 ▲   76 ●   437 ■   466 ■

165 ●   174 ▲   76 ●   128 ●   450 ■

200 400

126 ▲   116 ●   178 ▲   126 ●   239 ■   416 ■

107 ■ 110   176 ●   143 ●   100 ▲   87 ●   169 ■

110

164 ▲   180 ●   82 ●   132 ▲   87 ●   194 ▲

43°50'   — ■

111 ▲   107 ●   144 ●   74 ●   82 ●   100 ■

99 ▲   108 ●   170 ▲   117 ●   79 ▲   419 ■

110   110

84 ●   113 ■   92 ●   91 ●   104 ▲   107 ■

110
200   200   400

94 ■   228 ■   436 ■   134 ■   452 ■

400

469 ■

43°40'

BAY CITY

LOWER SAGINAW BAY

MILES
0 1 2 3 4 5 6 7 8 9

N

83°50'   83°40'   83°30'

Figure 13.   Eh of surface sediments (April 1975).

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within depositional basins is typical of the sedimentary environments of the Great Lakes. Lower pH and Eh values are associated with fine-grained, organic rich, comparatively reducing sedimentary materials.
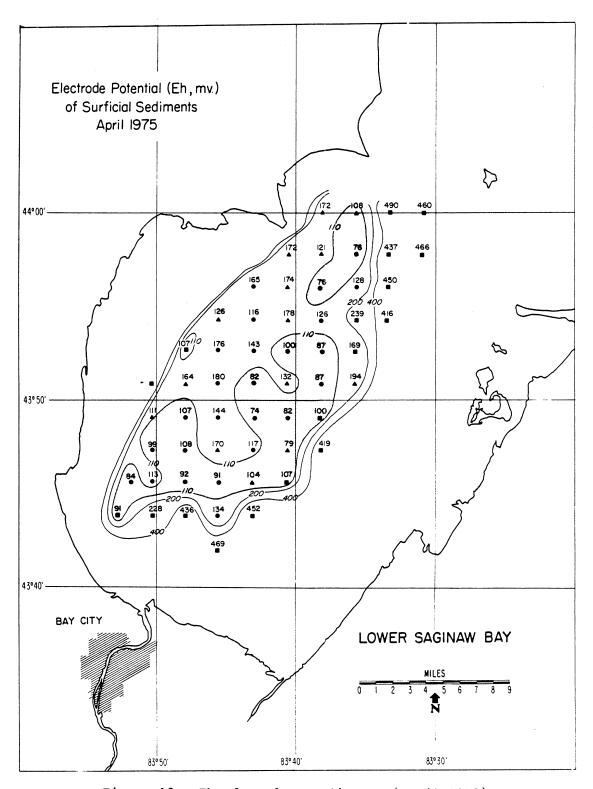
The distribution of inorganic carbon (Fig. 14) exhibits an enhanced concentration in the southwest end of the mud deposit. This trend is reflected in the distribution of calcium (Fig. 15) and magnesium (Fig. 16). The association of these constituents as well as their ratios provide presumptive evidence for preferential deposition of dolomitic materials in that area of the lower bay. The distribution of organic carbon in surface sediments (Fig. 17) contrasts markedly with those of the calcium element group. Organic carbon ranges from less than 1% to greater than 5% over the lower bay, with maximum concentrations tending to occur in deepest areas of the bay. Iron (Fig. 18) exhibits a similar pattern. Metals such as lead, zinc, and copper (which in surface sediments may be partly of anthropogenic origin) have distributions which are very similar to the distribution of iron. The distribution of lead is provided as an example in Figure 19. Concentrations range from less than 20 ppm in regions outside the mud deposit (sand/gravel) to greater than 80 ppm at several isolated sites within the depositional zone. In contrast to the above three contaminant metals, another, cadmium, has a distribution (Fig. 20) which is dissimilar to the iron group but resembles more closely the distribution of the calcium family constituents. The weaker association of cadmium with the iron-organic carbon group also occurs in surface sediments in the southern part of the main lake (Robbins 1980). The similarity of the distribution of iron in surface sediments to that of other elements is summarized in Figure 21 in terms of ordered correlation coefficients. Note that total iron exhibits the best

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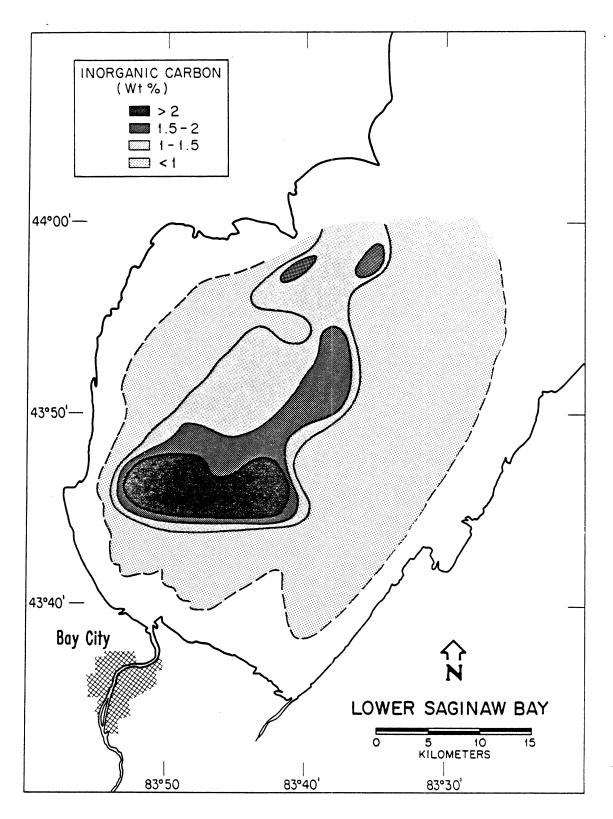
Figure 14.   Inorganic carbon in surface sediments (1-2 cm).

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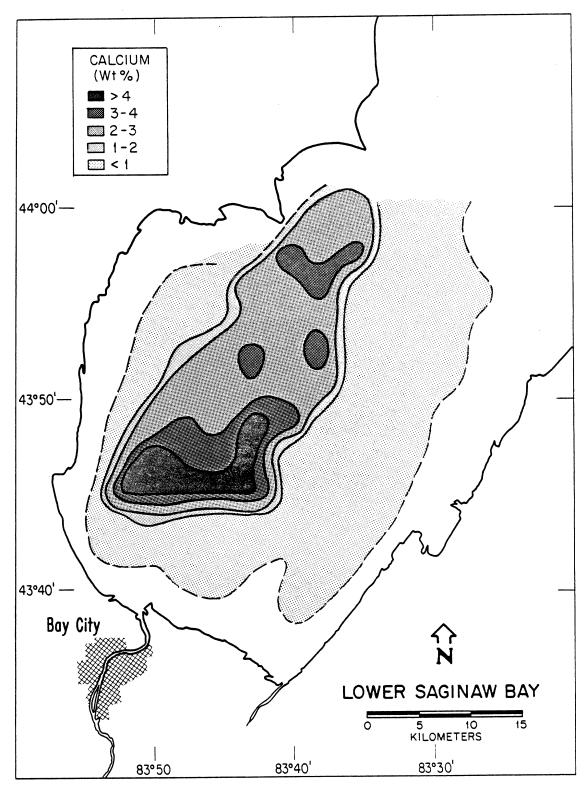
Figure 15. Calcium in surface sediments (1-2 cm).

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Figure 16. Magnesium in surface sediments (1-2 cm).

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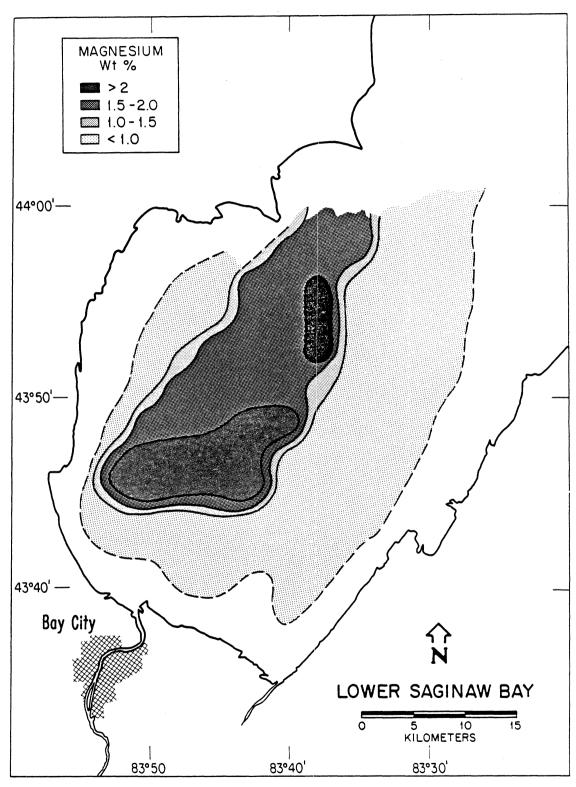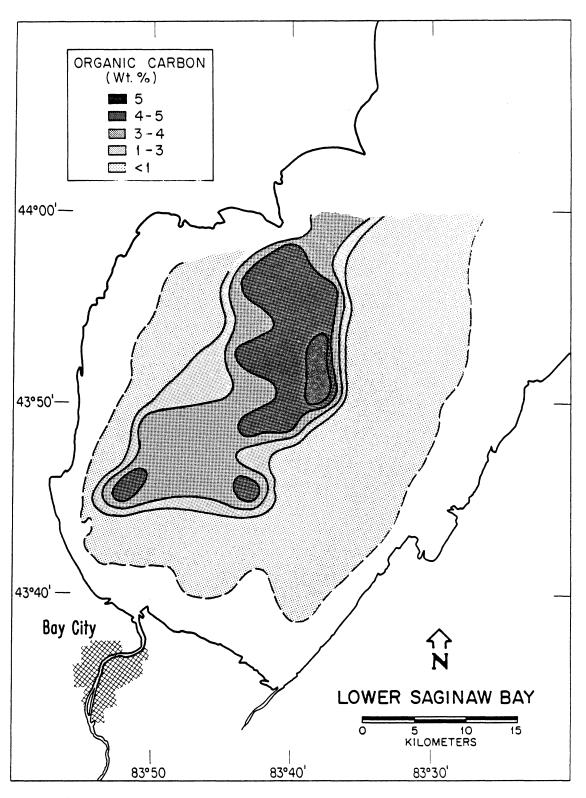Figure 17. Organic carbon in surface sediments (1-2 cm).
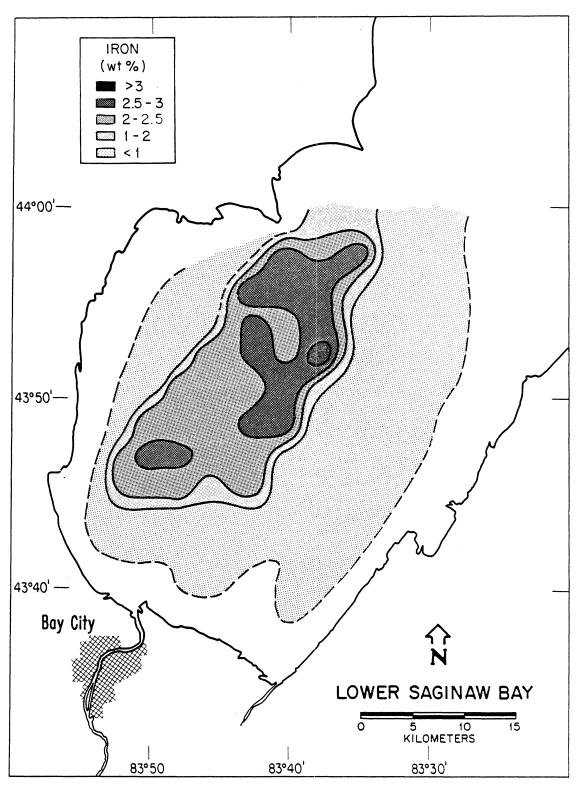
Figure 18. Iron in surface sediments (1-2 cm).

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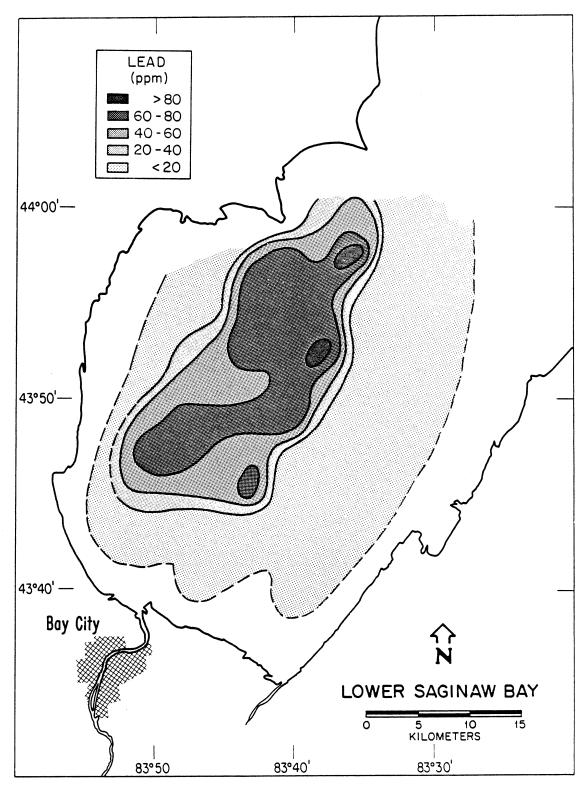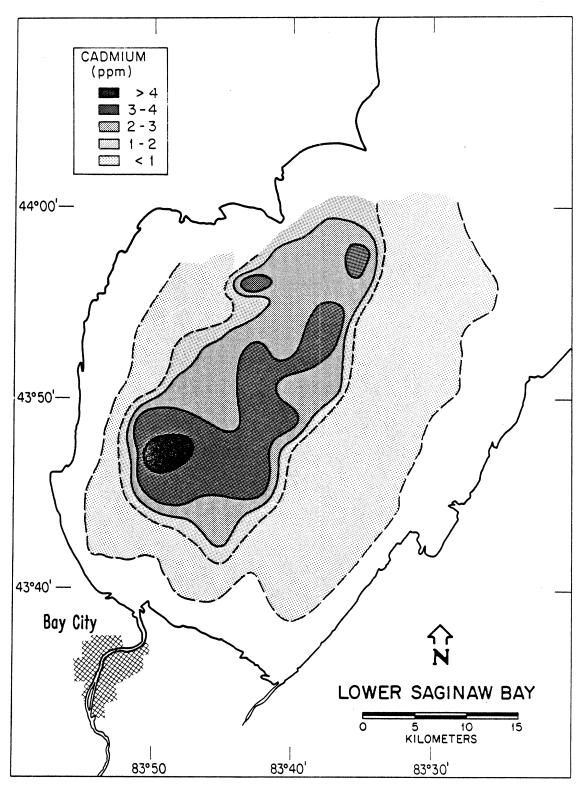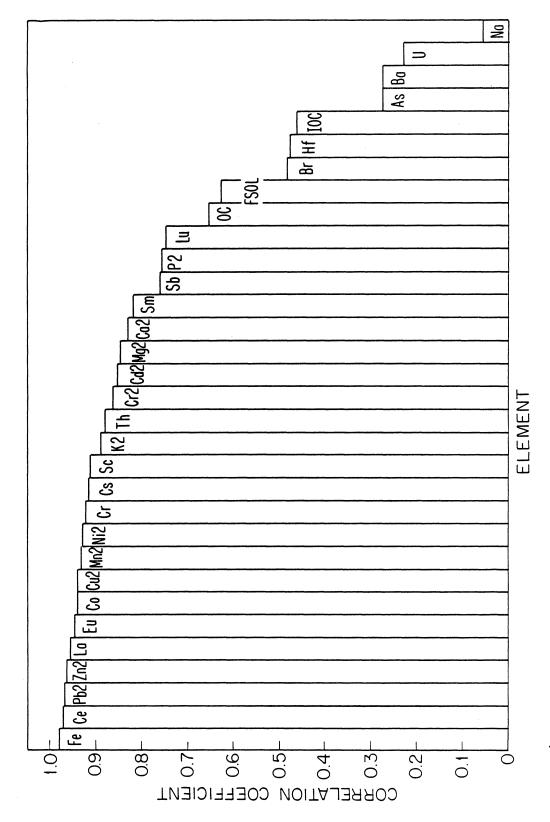Figure 19. Lead in surface sediments (1-2 cm).

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Figure 20. Cadmium in surface sediments (1-2 cm).

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Figure 21. Correlation between organic carbon and other elements in surface sediments.

correlation with acid soluble iron (Fe2) (r = 0.96 for N = 33). The elements

Pb, Zn, Cu, Mn, and Ni are all well correlated with iron while organic carbon

is comparatively less well-correlated in this environment. In contrast, in

surface sediments of the main lake, both iron and organic carbon are

significantly better correlated (Robbins 1980). Reasons for this difference

are unclear; however, a possible explanation is that the hydrodynamic

properties of iron and organic carbon-containing particulate matter may tend

to be more similar in deep water depositional environments remote from

allochthonous sources. It should also be noted that the inorganic carbon

content of surface sediments is more poorly correlated with calcium and

magnesium in sediments of Saginaw Bay than in sediments of the main lake

(Robbins 1980).

The surface sediment composition data are summarized in Table 1. Values

are in micrograms/gram (ppm) unless noted. The index 2 following an element

symbol (e.g., Fe2) indicates a concentration based on AAS analysis of acid

extracts. Elements without this index were determined by neutron activation

analysis of whole sediment. The extent of variability of the concentrations

is indicated by the ratio of the standard deviation of the values to the

average (coefficient of variation). This ratio is shown versus element in

Figure 22. Two major groups of elements may be distinguished: those with

coefficients greater than 0.4 and generally (with the exception of As) in the

range of 0.4-0.6, and those with values below 0.4, generally occurring within

a somewhat narrower range from about 0.25 to 0.35. Elements falling within

the high variability group include the calcium family constituents and the

contaminant metals group as determined from acid extracts. The low

variability group includes the rare earth elements, elements which are not

TABLE 1. Summary of surface concentration data.

Element	Range Minimum	Maximum	Average	Standard Deviation	Ratio*	Number of Samples
FSOL(%)	1.40	54.6	27.7	10.3	0.372	34
IOC(%)	0.110	2.49	1.42	0.619	0.437	29
OC(%)	0.320	5.21	3.47	1.14	0.330	28
As	1.14	60.2	16.6	13.5	0.814	35
Ba	183	551	422	82.9	0.196	35
Be	1.42	46.7	15.1	7.77	0.513	35
Ca2(%)	0.012	4.87	2.35	1.48	0.628	46
Cd2	0.170	4.32	2.40	1.22	0.507	33
Ce	7	55.6	41.1	11.1	0.270	35
Co	1.25	11.1	8.22	2.29	0.278	35
Cr	5.67	106	71.6	21.8	0.304	35
Cr2	8.93	173	63.5	36.8	0.508	46
Cs	0.216	5.15	3.25	1.05	0.323	35
CsR	0.110	7.04	2.97	1.42	0.479	35
Cu2	0.720	49.7	25.5	15.9	0.624	45
Eu	0.206	1.12	0.895	0.222	0.248	35
Fe(%)	0.310	3.43	2.38	0.686	0.288	35
Fe2(%)	0.026	3.21	1.78	0.948	0.532	46
Hf	0.880	9.19	5.60	1.51	0.269	35
K2(%)	0.104	1.23	0.652	0.247	0.379	33
La	5.13	31.9	24.2	6.30	0.269	35
Lu	0.044	0.423	0.283	0.075	0.264	35
Mg2(%)	0.020	5.56	1.54	1.05	0.682	46
Mn2	20	964	496	298	0.602	46
Na	4,020	9,090	6,550	1,130	0.172	35
Ni2	3.10	66.5	31.9	17.5	0.548	44
P2	187	2,100	1,330	486	0.366	26
Pb2	3.20	87.5	45.3	26.9	0.593	44
Sb	0.089	0.957	0.522	0.167	0.320	35
Sc	0.640	12.3	8.80	2.67	0.304	35
Se	0.574	3.00	1.76	0.474	0.269	35
Sm	0.770	5.28	3.76	1.08	0.287	35
Th	0.802	8.57	6.28	1.79	0.286	35
U	0.249	5.00	1.41	0.918	0.650	35
Zn2	4.90	188	96.3	56.2	0.584	45

Values in μg/g unless indicated. *Ratio = SD/mean = coefficient of variation.
FSOL = fraction soluble in acid; IOC = inorganic carbon; OC = organic carbon;
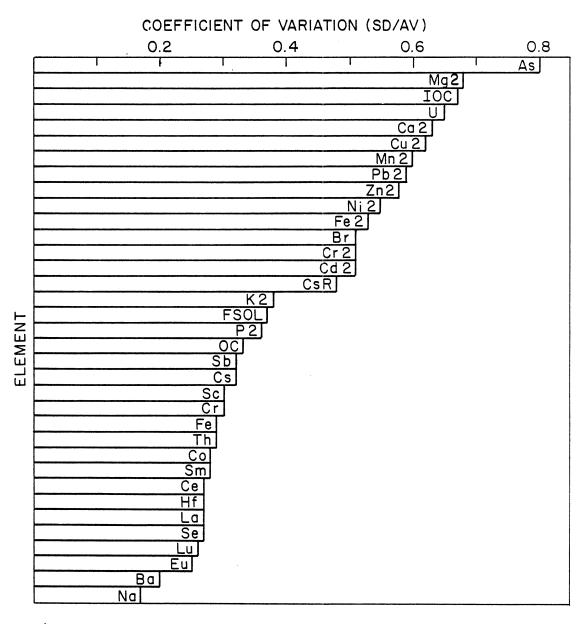CsR = radiocesium (Cs-137).

COEFFICIENT OF VARIATION (SD/AV)

Figure 22. Relative variability in concentrations of elements in
surface sediments (see text).

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likely to be contaminants and (where comparison is possible) the whole sediment concentrations of elements whose acid extract concentrations fall in the high variability group (e.g., Fe/Fe2, Cr/Cr2, and Cs/CsR).

A comparison of the concentration of elements in surface sediments of the lower bay with those in surface sediments in the southern part of Lake Huron is provided in Table 2. It can be seen that, generally, concentrations are lower in the bay mud deposits. A regression of ln C_{SB} vs ln C_{SLH} yields the following relationship:

$$\hat{C}_{SB} = 0.71\ C_{SLH}^{1.03} \tag{1}$$

with r = 0.99 (N = 33). The mean ratio of C_{SB}/C_{SLH} is 0.77. Thus, on the average, concentrations in the mud deposit of the bay are 30% less than in mud deposits in southern Lake Huron, presumably because of the greater dilution of bay sediments by inert (quartz/clays) materials. If the effects of this dilution are taken into account, only a few elements have significantly different average concentrations in the bay relative to the open lake. Most notable is whole-sediment chromium (Cr) which has an average concentration of 72 ppm. As the mean concentration in southern Lake Huron is 47 ppm, the above regression equation yields a predicted value of $0.71*47^{1.03} = 37.5$ ppm. Hence, if the effects of dilution are removed, concentrations of total chromium are 72/37.5 = 1.9 times higher in the bay than the lake. This relative enhancement is also seen in acid-soluble chromium, although to a lesser degree $(63/0.71*66^{1.03} = 1.2)$. Also occurring in relatively higher concentration (on an inert-material corrected basis) is organic carbon $(3.5/0.71*3.2^{1.03} = 1.5)$. The relative enhancement (or reduction) in the mean concentration of elements in the bay muds is shown in the last column of

TABLE 2. Comparison of average concentrations of elements in surface sediments of Saginaw Bay and southern Lake Huron.

Element*	Lower Saginaw Bay (C_{SB})	Southern Lake Huron** (C_{SLH})	Ratio of means (C_{SB}/C_{SLH})	Relative Enhancement ($\hat{C}_{SB}/C_{SB}$)
FSOL(%)	28	31	.90	1.15
IOC(%)	1.4	2.4	.58	0.80
OC(%)	3.5	3.2	1.08	1.48
As	16	27	.61	.78
Ba	422	432	.98	1.14
Br	15	51	.29	.37
Ca2(%)	2.4	2.7	.89	1.22
Cd2	2.4	2.9	.83	1.13
Ce	41	54	.76	.95
Co	8.2	10.6	.77	1.02
Cr	72	47	1.53	1.92
Cr2	63	66	.95	1.18
Cs	3.3	3.6	.91	1.24
Cs137	3.3	7.7	.42	.56
Cu2	25	37	.67	.85
Eu	.90	1.1	.81	1.15
Fe(%)	1.8	2.4	.75	1.03
Fe2(%)	2.4	3.1	.77	1.05
K2(%)	.65	.68	.96	1.36
La	24	31	.77	.98
Lu	.28	.33	.85	1.24
Mg2(%)	1.5	2.0	.75	1.03
Mn2	.050	.13	.38	.58
Na	6,550	7,300	.90	.97
Ni2	31.9	50.6	.63	.79
P2	1,330	1,500	.88	1.00
Pb2	45.3	73.6	.62	.76
Sb	.52	.87	.60	.85
Sc	8.80	11.2	.79	1.03
Sm	3.76	5.23	.72	.96
Th	6.28	8.24	.76	1.00
U	1.41	2.79	.50	.69
Zn2	96.3	116.3	.83	1.01

*Values in μg/g unless indicated. **From Robbins (1980).

Table 2. Some elements, notably Br, Cs-137, Mn2, and U are significantly less in the bay muds even after correction for dilution. Reasons for this reduction are not clear. In the case of the radionuclide, Cs-137, which enters the lake primarily from atmospheric fallout, the reduction may be attributable to focusing effects. Cesium-137 deposited over a wide area (lake surface) accumulates in comparatively limited areas of the lake bottom. In the bay, the area of accumulation is comparable to the area of initial deposition. Also, more Cs-137 may be exported to the open lake from shallow bay waters through resuspension.

Coefficients of correlation between contaminant metal concentrations (namely Cd, Cr, Cu, Ni, Pb, and Zn), provided in Table 3, illustrate their very high degree of similarity in areal distribution within surface mud deposits. In all cases but the pair Zn-Cr, for which r = 0.89, values of the correlation coefficient exceed 0.9 for $N \geq 32$ in the case of Cd and $N \geq 43$ for the other element pairs, not involving Cd. Analysis of one contaminant element in surface sediments serves to establish levels of the others with a high degree of confidence.

TABLE 3. Correlation coefficients for pairs of contaminant metal concentrations (acid soluble) in surface sediments.

	Cd	Cr	Cu	Ni	Pb	Zn
Cd	1	.90	.94	.91	.91	.92
Cr	.90	1	.93	.91	.94	.89
Cu	.94	.93	1	.94	.97	.98
Ni	.91	.91	.94	1	.97	.95
Pb	.91	.94	.97	.97	1	.99
Zn	.92	.89	.98	.95	.99	1

For Cd $N \geq 32$; for other elements $N \geq 43$.

As both grain size distribution and concentration data are available for surface sediments, some inferences may be made concerning the association of elements with sediment grain size. Ideally, the elemental composition of sediment size fractions should be measured, but such an approach is beyond the scope of this study. However, to the extent that the concentration of an element in sediments of a well-defined size range (e.g., 3 to 4 phi units) is independent of location over the lower bay, the concentration may be inferred by statistical analysis of a sufficiently large concentration-grain size data set. If f_i is the fraction of the total dry weight of sediment which is in the ith size class, and the concentration of a certain element in that size class is C_i, then the measured concentration in the sample is

$$C = \sum_{i=1}^{N} C_i f_i.$$ (2)

If C_j is the measured concentration in the jth sample, then the assumed independence of C_i on location means that

$$C_j = \sum_{i=1}^{N} C_i f_{ij}$$ (3)

where f_{ij} is the fraction of the total sediment dry weight in the ith size class at the jth location. It is further assumed that the dependence of C'_i on mean grain size in each size class (ϕ_i) is essentially Gaussian so that,

$$C_i = C_{max} e^{-(\phi_i - \phi_m)^2 / 2\sigma_\phi^2}$$ (4)

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A nonlinear least squares routine was used (Dams and Robbins 1970) to determine values of the three parameters (C_{max}, ϕ_m, and σ_ϕ) for each element using the surface concentration data and grain size data. The results are presented in Table 4 and Figure 23. It can be seen that the elements (Fe2, Fe, Pb2, Zn2, and Br) are apparently associated with the smallest mean grain sizes (greater than 10 phi units). These elements not only are associated with particularly fine grained sediments but concentrations are distributed over a wider range of sizes (especially Fe2, for which the value of σ_ϕ is 6.3 phi units). The model concentrations for these elements shown in Figure 23 indicate that Fe2 is, in fact, not strictly Gaussian, in the sense that the apparent position of the maximum is beyond the range of the data. Also shown in Figure 23 (upper panel) is the correlation of the measured concentration with each size class. Generally, for all elements (including those shown), correlations are high (>0.7, N = 30) for grain sizes greater than 7 phi. Below 7 phi units, the correlation decreases rapidly, reaching zero at 4 phi units and remains zero or negative for even lower phi values (larger grain sizes). Thus, the measured concentrations of all elements of this study are derived from partial concentrations of the element on grain sizes smaller than about 60 microns (4 phi). The presence of materials with grain sizes greater than 4 phi (coarse silt) merely serves to dilute sediments with inert constituents (inert with respect to elements determined in this study). In the case of Fe2 and Pb2 (Fig. 23), the correlations vs. grain size in the interval beyond 7 phi units are comparable, although the correlations with lead remain slightly higher. The behavior of calcium, however, is significantly different. For this element, the maximum correlation occurs around 7-8 phi units and drops significantly for smaller particle sizes

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TABLE 4. Grain size/concentration model parameters.

Element	Cmax*	ϕ_m (phi units)	σ_ϕ (phi units)	Correlation Coefficient**	Number of Samples
FSOL	209.	7.1	0.66	.51	34
IOC	9.65	6.8	0.68	.52	29
OC	205.	8.0	0.25	.65	28
Br	76.6	13.0	2.2	.49	35
Ca2	19.7	6.7	0.64	.81	46
Cd2	7.8	7.8	1.8	.86	33
Ce	93.9	8.1	2.2	.67	35
Co	23.1	8.0	1.8	.70	35
Cr	266.	7.6	1.4	.70	35
Cr2	142.	10.8	3.8	.80	46
Cs	7.82	11.0	3.0	.68	35
CsR	159.	8.8	0.21	.81	35
Cu2	318.	7.0	0.50	.89	45
Eu	1.63	8.4	2.8	.62	35
Fe	4.93	10.5	3.2	.72	35
Fe2	9.25	18.4	6.3	.87	46
Hf	9.72	6.2	2.2	.41	35
La	52.6	8.4	2.4	.69	35
Lu	0.65	7.6	2.0	.56	35
Mg2	24.6	8.2	0.52	.82	46
Mn2	1,200.0	8.4	2.5	.83	46
Na	10,000.	5.4	2.7	.44	35
Ni2	168	7.1	1.1	.85	44
P2	3,500.	8.4	2.1	.56	26
Pb2	128.	10.3	2.8	.91	44
Sb	0.99	9.4	3.0	.54	35
Sc	36.8	7.3	1.2	.69	35
Sm	16.4	6.9	1.0	.69	35
Th	21.9	7.3	1.4	.71	35
U	3.3	7.0	1.8	.25	35
Zn2	284.	12.0	3.6	.90	45

* Units are identical with those in Table 1.

**The coefficient of correlation between measured and predicted values of surface concentrations.

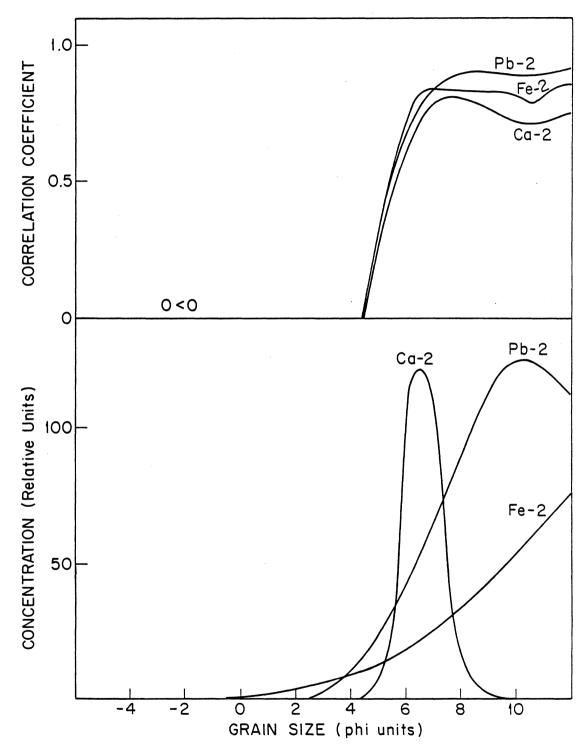Figure 23. Model concentrations of calcium, iron, and lead as a
function of grain size (see text).

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(ϕ = 9). This result, which does not depend on any complex model analysis, suggests an association of Ca with a narrower range of grain sizes than Pb2 and Fe2. This is borne out by the concentration model analysis as well. The distribution of Ca as well as the other calcium family elements (FSOL, Mg, IOC) peaks at a distinctly lower value of phi (ϕ = 6.7) and has a very narrow grain size range (0.64 phi units). The model concentration of calcium vs. grain size (Fig. 23) indicates that this element is associated with fine silt (8-16 micron dia) whereas both lead and iron are associated with fine clays (<2 micron dia). Other elements are relatively undistinguished in terms of grain size, but several have relatively narrow grain size ranges (like the Ca group) for reasons which are not clear. These include: organic carbon, Cs-137 (CsR), and Cu2.

VERTICAL DISTRIBUTION OF ELEMENTS

The vertical distribution of FSOL (fraction soluble on acid treatment) and selected acid-soluble major and minor elements are illustrated in Figures 24 through 34. The behavior of FSOL as exemplified in Figure 7 for a core at station 40 is characteristic of its behavior in other cores. As seen in Figure 24, FSOL at first decreases with increasing sediment depth (through zones 1-2) and increases once again in zone 4. Note that the porosity remains more or less constant in zone 4 for the cores used for illustration (Fig. 9). Both calcium and magnesium (Figs. 25 and 26, respectively) follow a similar trend, decreasing within zones 1 to 3 but rising dramatically (up to a factor of 4) within zone 4. The concurrent rise in both magnesium and calcium suggests an increase in the amount of dolomitic materials within zone 4. The behavior of iron contrasts strongly with that of FSOL, Ca, and Mg.
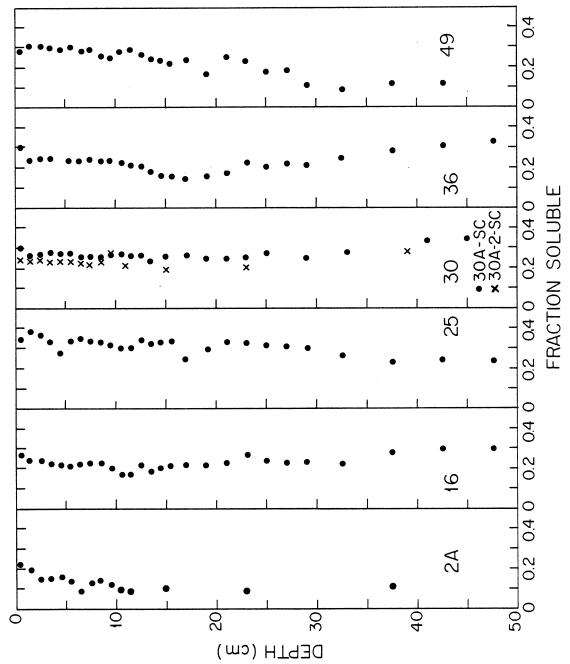
39

Figure 24. Vertical distribution of fraction soluble in selected sediment cores (see text).

Figure 25. Vertical distribution of calcium in selected sediment cores.

Figure 26. Vertical distribution of magnesium in selected
sediment cores.

Figure 27. Vertical distribution of iron in selected sediment cores.

Figure 28. Vertical distribution of manganese in selected sediment cores.

Figure 29. Vertical distribution of chromium in selected sediment cores.

Figure 30. Vertical distribution of copper in selected sediment cores.

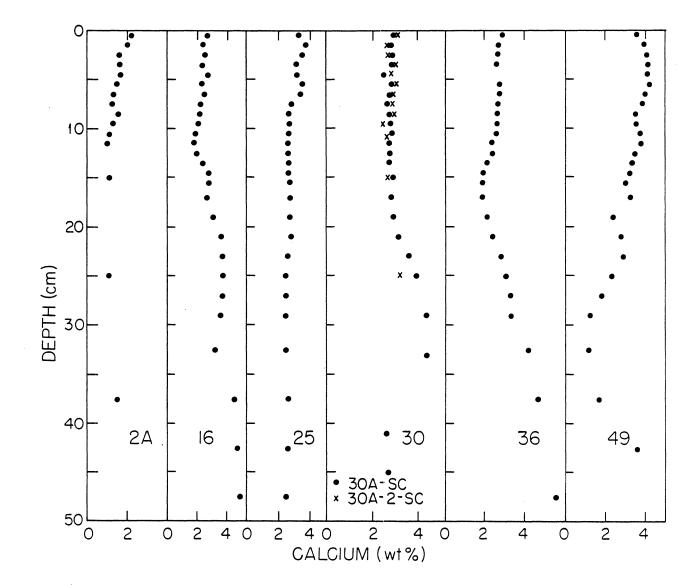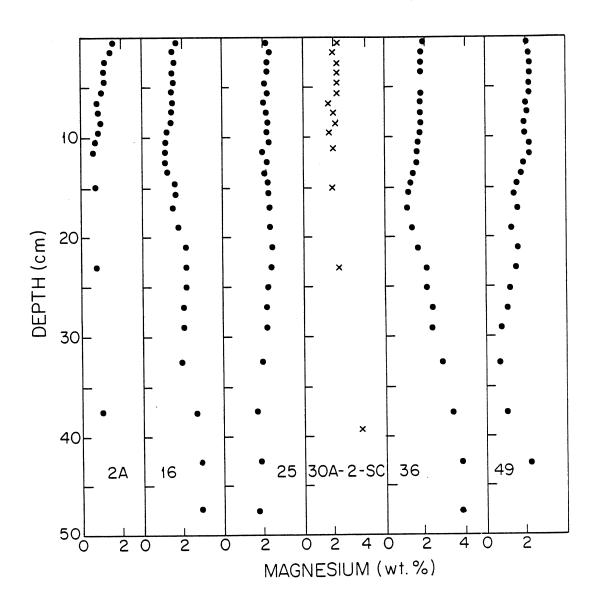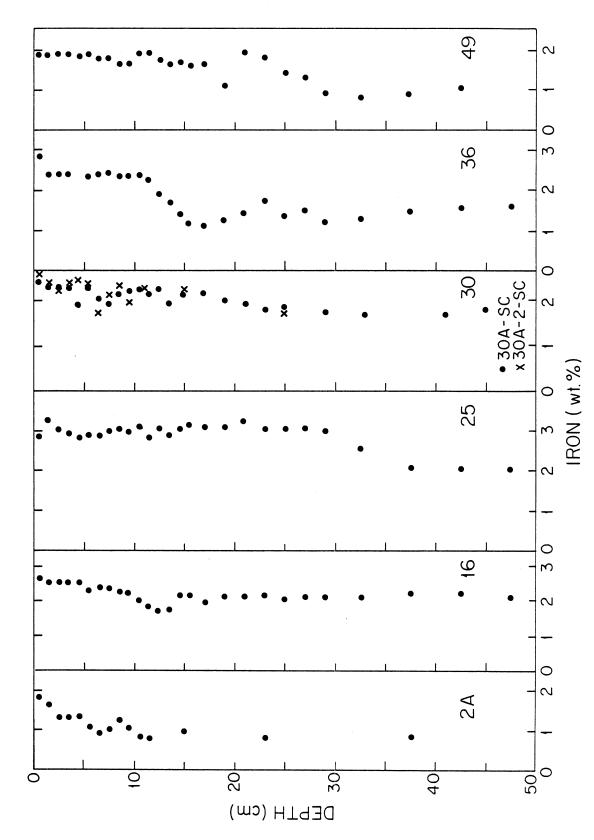Figure 31. Vertical distribution of lead in selected sediment cores.

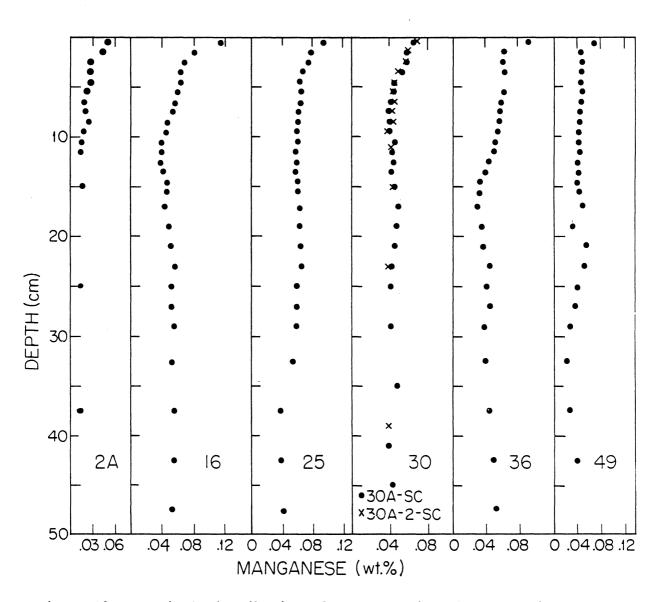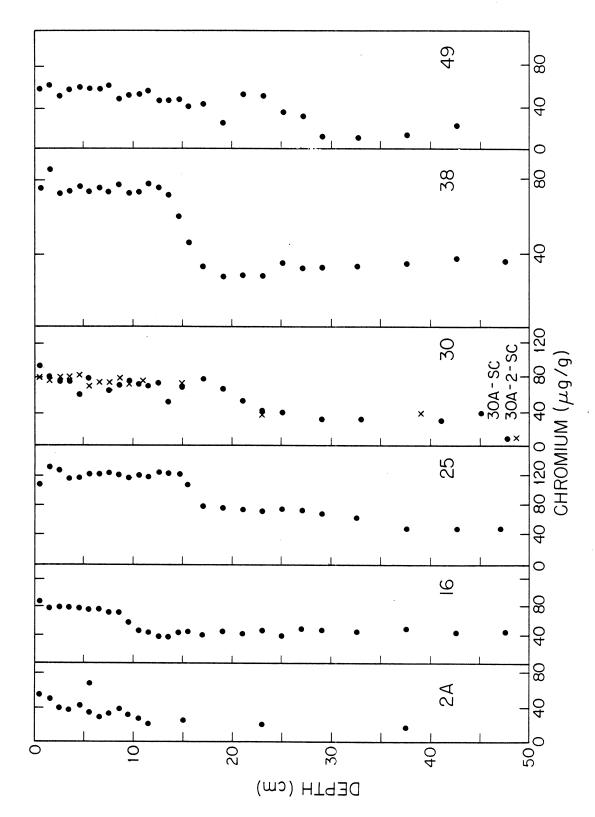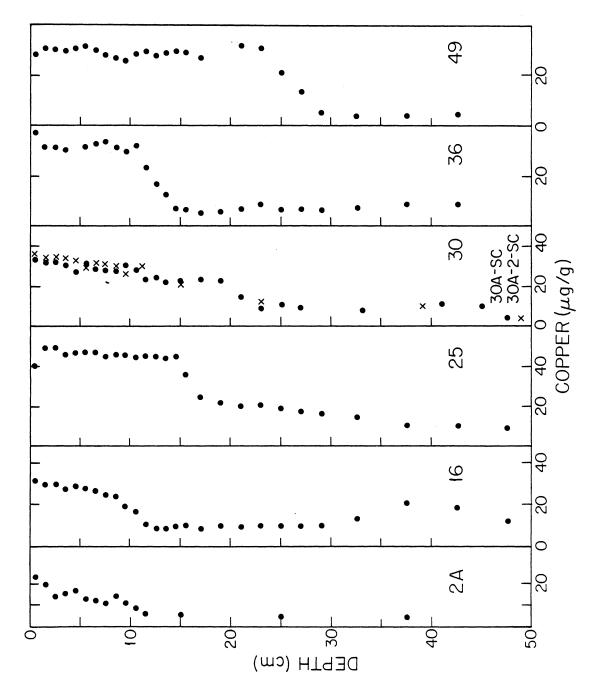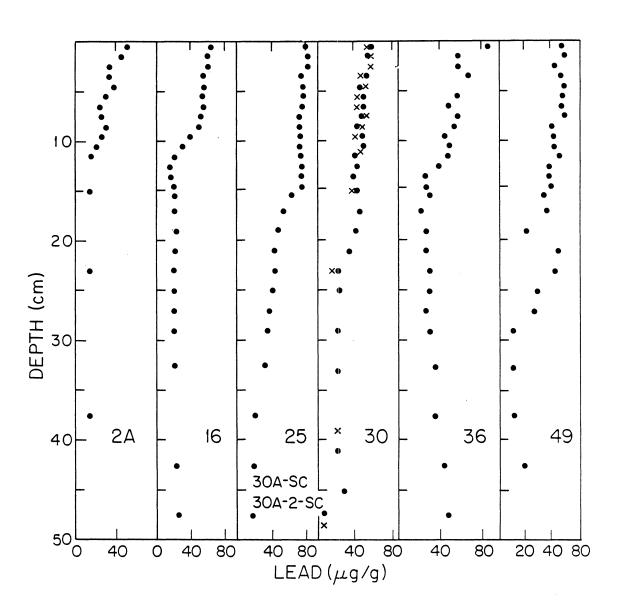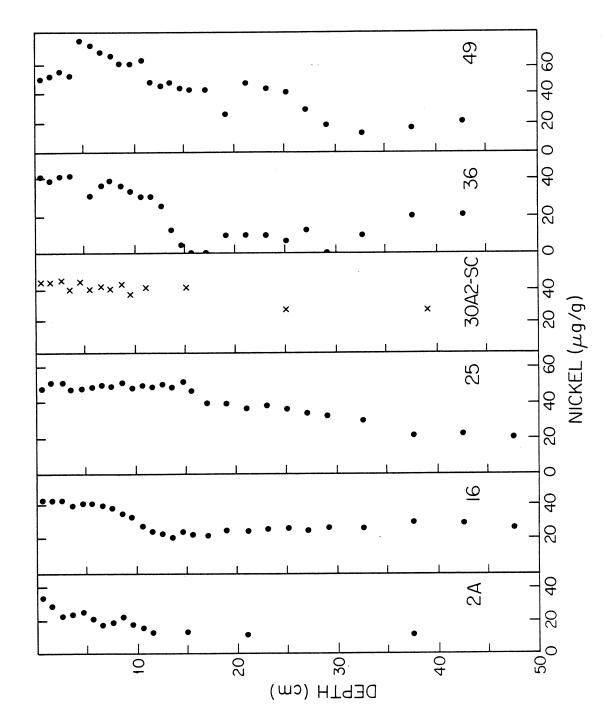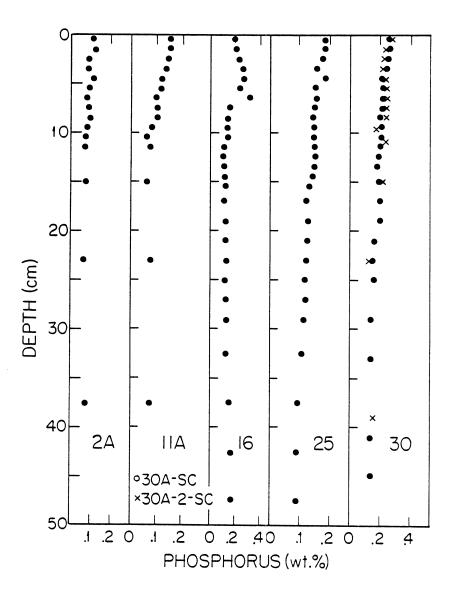Figure 32. Vertical distribution of nickel in selected sediment cores.

Figure 33. Vertical distribution of acid soluble phosphorus in selected sediment cores.
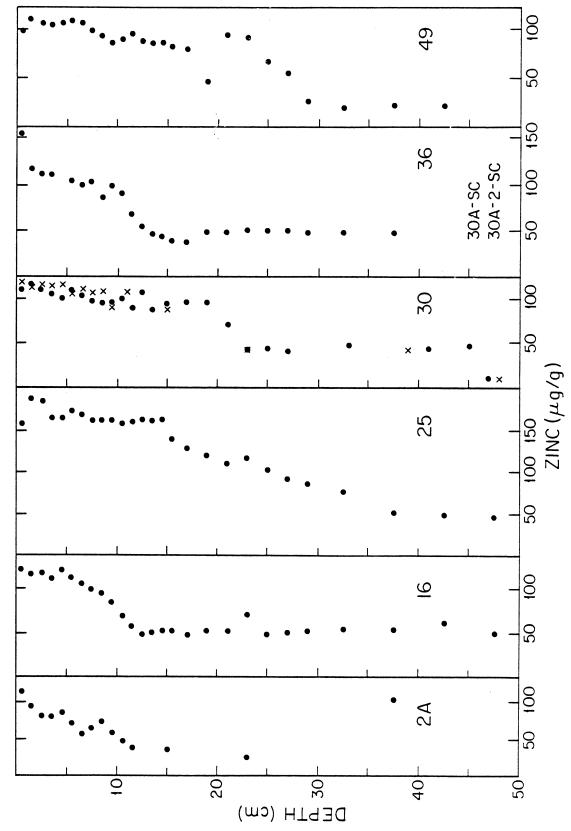
Figure 34. Vertical distribution of acid soluble zinc in selected sediment cores.

As seen in Figure 27, the concentration of Fe tends to be constant within zones 1-2, decreases abruptly within zone 3, and remains constant within zone 4. For manganese (Fig. 28), the behavior is similar to that of iron except for a significant increase within zone 1 (the flocculent material in the upper 1 cm). The minor elements (Figs. 29-34), for the most part, exhibit the same behavior as iron: constant or slightly decreasing concentrations in zones 1-2, an abrupt decrease in zone 3, and again constant concentrations in zone 4. These profiles suggest that zones 1 and 2 are comprised of sediments containing recent anthropogenic constituents overlying older, uncontaminated materials. As the minor constituents are of relatively uniform concentration within these upper sediments, zones 1 and 2 appear to be either recent overlays of translocated materials or materials thoroughly reworked to a depth of well-defined extent which varies systematically with location (Fig. 38). The notion of well-mixed recent materials comprising zones 1-2 is further supported by radiometric evidence discussed below.

The extent of enrichment of elements within the upper sediment zones (1 and 2) relative to underlying sediments (zone 4) is given in Table 5 in terms of the ratio of element concentrations in zone 2 to concentrations in zone 4. On the average, concentrations of Cu, Pb, and Zn are four times higher in zone 2 than in zone 4. Elements Cr, Ni, and Mn are twice as high, and the remaining elements, while possessing elevated concentrations relative to underlying sediments, do not exhibit a major degree of enrichment. At least part of the enrichment is due to the increase in inert (quartz?) constituents in underlying sediments (zone 3 and possibly 4). To eliminate effects of dilution by inert materials, the degree of enrichment may be recalculated in terms of the concentrations of elements on a weight soluble

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TABLE 5. Surface to deep layer concentration ratios in sediment cores from Saginaw Bay.

Site* Number	Constituent											
	FSOL	Ca	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	Zn
2	1.9	2.0	2.5	3.7	2.1	1.5	2.0	3.3	2.7	1.6	3.2	2.5
11	1.5	1.3	2.1	2.8	1.6	1.3	2.0	2.8	2.3	2.5	3.2	2.5
16	.84	0.53	1.7	3.0	1.2	1.0	0.54	1.6	1.7	1.3	2.7	2.2
25	1.4	1.4	2.5	3.6	1.6	1.3	1.2	1.9	2.2	2.1	4.7	3.5
28	1.0	–	–	5.0	–	–	–	–	2.0	–	2.7	4.0
29	.65	–	–	3.0	–	–	–	–	1.2	–	2.0	2.4
30	1.0	0.71	2.6	3.7	1.4	1.4	0.86	1.5	1.6	1.9	2.6	2.6
36	.84	0.58	3.2	4.7	1.9	1.6	0.54	1.7	4.0	–	2.0	3.0
38	1.6	1.2	2.3	6.1	1.8	2.5	1.2	2.1	2.8	–	5.0	4.5
40	1.4	0.63	3.1	4.9	1.7	2.5	0.70	2.7	3.6	–	4.0	4.1
43	1.7	–	–	4.5	–	–	–	–	3.7	–	5.5	6.3
49	1.8	2.0	2.7	2.5	1.9	2.3	2.2	2.0	2.8	–	4.6	5.0
Mean		1.1	2.4	4.0	1.7	1.7	1.2	2.2	2.6	1.9	3.5	3.6

*See Fig. 2 for locations.

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basis. If C_s is the concentration of a given element in surface sediments in g/g, then the concentration on a weight soluble basis is given by

$$C_s' = C_s / F_s \qquad (5)$$

where F_s = Fraction soluble (g soluble / g total)

= FSOL

The sediment enrichment factor is then calculated as

$$SEF = \frac{C_s' - C_d'}{C_d'} \left. \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \right\} \qquad (6)$$
$$= \frac{C_s \, F_d}{C_d \, F_s} - 1$$

where C_d is the characteristic (mean) concentration of an element in deep sediments (zone 4) and $C_d' = C_d/F_d$ as above. When the concentration of an element on a weight soluble basis is the same in surface and underlying sediments, SEF = 0.0. Kemp et al. (1974), who introduced the concept of the SEF, used aluminum rather than FSOL as a basis for normalizing concentration values. SEF values are given in Table 6 for selected cores in terms of percent enrichment. Elements divide into four discrete categories of enrichment: (1) Cu, Pb, and Zn have average SEFs close to 200%, (2) Cr and Ni have values around 100%, (3) Mn, P, Fe, K have values of around 50%, and (4) Mg and Ca are negatively enriched by about -15%. Because major enrichment of Mn occurs within zone 1 the calculated SEF is sensitive to details of the sampling and averaging. Use of only zone 1 (0-1 cm or less) in the estimate of the average would greatly (x2 - x3) increase the SEF for Mn.

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Included in Table 6 are mean SEFs for sediments of southern Lake Huron. A comparison of values indicates that, while enrichments of Pb and Zn are comparable in the bay and open lake sediments, the elements Cr, Cu, and possibly P are significantly more enriched in sediments of the bay. Thus, while dilution of anthropogenic constituents by inert materials in bay sediments suppresses concentration values, and while removal of such effects by regression techniques indicates concentrations in surface sediments undistinguished from the open lake, it is evident that, relative to sediments originally present (underlying materials), surface materials are significantly more enriched in copper and chromium. This contrast with the open lake suggests the importance of local sources (tributary?) of these elements.

If the enrichment of elements in zones 1 and 2 (Mn excepted) is due solely to anthropogenic loadings, then the excess accumulation at each location may be calculated as follows:

$$\text{Excess accumulation } (\mu g/cm^2) = \sum_{i=1}^{n} (C^i_{total} - C_{Bg})w^i \tag{7}$$

where C^i_{total} = the concentration of a given element in the ith sediment interval ($\mu g/g$), C_{Bg} is the background concentration of the element and w^i is the mass per unit area of sediment in the ith interval (g/cm^2). It must be emphasized that the excess accumulation is truly the anthropogenic element storage only if C_{Bg} is the same in zone 2 as it is deeper in the core (i.e., in zones 3 and 4 below the enriched layer). Values of the excess accumulation are given in Table 7 for selected cores. A comparison of these values with those for southern Lake Huron provides a striking contrast. Far more excess

TABLE 6. Sediment enrichment factors (SEF in %) for cores from Saginaw Bay.*

Site* Number	Constituent										
	Ca	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	Zn
2	5.2	32	95	10	-21	5	74	42	-16	68	32
11	-13	40	87	7	-13	33	87	53	66	113	67
16	-37	102	257	43	19	-36	90	102	54	221	162
25	0	79	157	14	-7	-14	36	57	50	236	150
28	-	-	499	-	-	-	-	100	-	170	300
29	-	-	361	-	-	-	-	85	-	207	270
30	-29	160	270	40	40	-14	50	60	90	160	160
36	-31	280	450	130	90	-36	103	376	-	140	260
38	-25	44	281	13	56	-25	31	75	-	212	181
40	-55	121	250	21	79	-50	93	157	-	190	193
43	-	-	164	-	-	-	-	120	-	123	270
49	11	50	40	6	28	22	11	60	-	160	180
Mean (SB)	-19	100	230	31	30	-13	64	110	50	180	190
Mean (SLH)**	+18	-3	40	-1	-9	-7	126	55	0	220	105

*For the definition of SEF, see text (Eq. 6).
**Values for southern Lake Huron are from Robbins (1980).

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TABLE 7. Excess element accumulation in selected cores from lower Saginaw Bay ($\mu g/cm^2$).

Site Number	Element					
	Cr	Cu	Ni	P	Pb	Zn
2	97	54	60	1,620	61	230
11	71	40	52	1,100	81	160
16	130	68	59	3,700	140	230
25	460	230	190	4,500	340	690
28	–	150	130	–	270	600
29	–	100	60	–	200	380
30	340	140	130	2,936	200	460
36	120	150	150	–	150	320
38	180	130	130	–	220	420
40	460	220	200	–	290	570
43	320	230	160	–	340	720
49	630	350	580	–	470	1,064
Mean (SB)	280	160	160	2,800	230	490
Mean (SLH)*	0	19	25	0	75	94

*Data from Robbins (1980).

(anthropogenic) Cr, Cu, Ni, P, Pb, and Zn is stored per unit area in the lower

bay than in open lake sediments. How can this be reconciled with the

generally lower element concentrations in surface sediments of the bay?

Simply because the overlay of enriched sediments is generally of far greater

depth in lower bay deposits. Evidence provided below indicates that the

zoobenthos present in these deposits redistribute contaminants throughout a

considerable depth in the sediments. Thus, in the lower bay, contaminant

concentrations in surface sediments are apparently reduced as a result of two

important processes: (1) dilution by inert materials and (2) redistribution

of materials throughout a portion (up to $\sim$20 cm) of the sedimentary column.

An approximate estimate of the total excess storage of selected "anthro-

pogenic" elements in the lower bay is provided in Table 8. Insufficient data

are available to compute very accurate averages. However, an order of magni-

TABLE 8. Approximate total storage of anthropogenic metals in lower Saginaw Bay.*

Element	Mean Excess Accumulation (μg/cm^2)	Total Storage (metric tons)	Total Storage in Southern Lake Huron (metric tons)
Cr	280	1,500	$\simeq 0$
Cu	160	830	710
Ni	160	830	950
P	2,800	15,000	$\simeq 0$
Pb	230	1,200	2,400
Zn	490	2,500	2,900

*Based on acid soluble concentrations.

tude comparison indicates that amounts of Cu, Ni, Pb, and Zn stored in the lower bay are comparable to amounts stored in deposits of southern Lake Huron, which are roughly five times as extensive as those in the lower bay.

SEDIMENT MIXING AND SEDIMENTATION RATES

In the preceding discussion, it has been possible to investigate patterns of contaminant metal deposition, inter-element associations, and even total anthropogenic element loadings without reference to sedimentation rates. To gain information about the rates of contaminant deposition, however, it is necessary to associate a time scale with concentration profiles in individual cores. Two independent methods have been used for sediment geochronology in this report. The first relies on measurement of the vertical distribution of cesium-137 and the occurrence of a horizon corresponding to the onset of nuclear testing about 25 years ago. This method provides a measure of the average sedimentation rate over the past 25 years. The second method is based on the radioactive decay of lead-210 ($t_{1/2}$ = 22.26 years) following burial in sediments. In principle this method is capable not only of yielding average sedimentation rates over a period of roughly 100 years, but is capable of revealing changes in the rate of sedimentation over this period of time.

The computation of contaminant fluxes is sensitive to the interpretation given to individual profiles. This fact has been emphasized in a number of recent studies (Robbins et al. 1977, Robbins and Edgington 1975, Edgington and Robbins 1976, Robbins et al. 1978) which show that the mixing of surface sediments, probably by benthic organisms, has a significant influence on radioactivity and metal contaminant profiles and in the estimate of contaminant fluxes (Edgington and Robbins 1976). In the section below on cesium-137, the effects of sediment mixing on radioactivity and contaminant profiles are discussed.

Cesium-137

Cesium-137 is a uniquely anthropogenic radionuclide first introduced into the environment as a result of atomic weapons testing which began roughly 25 years ago. Many studies have now demonstrated the utility of cesium-137 for investigation of sedimentation processes in aquatic systems such as lakes and reservoirs. Cesium-137 is an especially useful tracer because its input to the lakes may be accurately inferred from atmospheric and precipitation radioactivity measurements (Sr-90) made for about a 20-year period within the watershed of the Great Lakes and elsewhere.

The time dependence of the input of this isotope is discussed in greater detail in the previous report (Robbins 1980). Most of the cesium-137 was introduced into the lakes during the period from 1958 to 1964. Thus, to a good approximation, the input is in the form of a pulse whose subsequent behavior in the water column and sediments serves to trace long-term aquatic transport processes. Studies by others have shown the residence time of cesium-137 in the water column to be very short (for details, see Robbins

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1980), about one year. Thus the radionuclide is rapidly removed from the water, and changes in its aqueous concentration mimic the history of atmospheric deposition as a result. As the hydraulic retention time of the lake is long (about 30 years) in comparison with the overall residence time of the radionuclide, the dominant process for removal of cesium-137 is particle scavenging and sedimentation. This inference is consistent with the known high affinity of radiocesium for certain clay minerals present in the water column. It is therefore expected that the flux of cesium-137 to the sediments would follow the time-dependence of aqueous concentrations as well as that of atmospheric inputs. While the flux may do so, profiles of cesium-137 do not, but are generally smoothed out both in open lake sediments (see Robbins 1980) and in those of Saginaw Bay as well.

As part of this and the previous report, a model has been developed to account for the discrepancy between observed and expected cesium-137 profiles. The details are presented in Robbins et al. (1977). The smearing is assumed to occur only in the sedimentary column and, as a result of the rapid steady-state mixing of sediments over a zone of fixed depths, at the sediment water interface. This depth is referred to as the mixing depth. It can be shown (Robbins et al. 1977) that if the activity of radiocesium added to the sediments at time t (with t = 0 corresponding to a very deep sediment layer) is $A_s(t)$, the expected cesium-137 distribution is given by:

$$A = A_m(T) \qquad z \leq s$$

$$A = A_m(T + (s - z)/\omega)\, e^{-\lambda}(z-s)/\omega \qquad z > s$$

and

$$A_m(t) = \gamma\, e^{-(\gamma + \lambda)t} \int_0^t e^{+(\gamma + \lambda)}\, A_s(\tau)\, d\tau \tag{8}$$

where $\gamma = r/s$, $t = T$ corresponds to the sediment water interface, and $\bar{\omega}$ is the sedimentation rate (cm/yr) neglecting the effects of compaction. λ is the radioactive decay constant for cesium-137 ($\lambda = 0.69315/t_{1/2}$; $t_{1/2} = 30.0$ years) and z is the depth below the sediment-water interface. The effects of compaction are automatically taken into account by expressing z in terms of the cumulative mass per unit area and ω in terms of the mass sedimentation rate ($g/cm^2/yr$). The mixing depth, in consistent units, is expressed in terms of mass/unit area.

A computer program was developed to find the value of the mixing depth, sedimentation rate, and surface activity $A_s(T)$ giving the best least squares fit of the above equation to the observed profiles. The results of the calculation are illustrated in Figure 35 for the distribution of cesium-137 in a core from station 10. The solid line represents the model distribution with values of 2.2 g/cm^2 for the depth of mixing and 0.11 $g/cm^2/yr$ for the sedimentation rate. In linear terms this mixed depth corresponds to about 10.5 cm and a sedimentation rate of about 0.53 cm/yr (a mean value for the upper 10 cm of sediment). The shaded area in Figure 35 is the distribution of cesium-137 expected if there were no mixing at this location but if the sedimentation rate remained the same. The effect of mixing is thus to drastically smear out the distribution. Distributions of cesium-137 in Saginaw Bay are in fact so dominated by mixing that often the peak (such as that seen at about 15 cm in the core at station 10) is completely absent. Such distributions provide little reliable sedimentation rate information but yield data on mixing depths. Profiles of cesium-137 in other cores are illustrated in Figure 36. It can be seen that the activity is smeared over an interval ranging from about 10 to 25 cm.
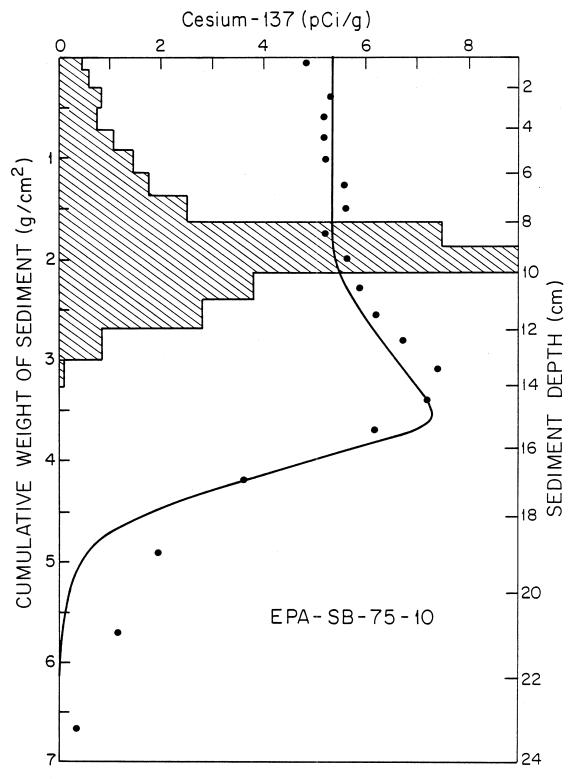
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Figure 35. Vertical distribution of cesium-137 in a sediment core at station 10. Also shown is a theoretical distribution based on the rapid steady-state mixing model (see text). The shaded region shows the distribution of cesium-137 expected in the absence of mixing.
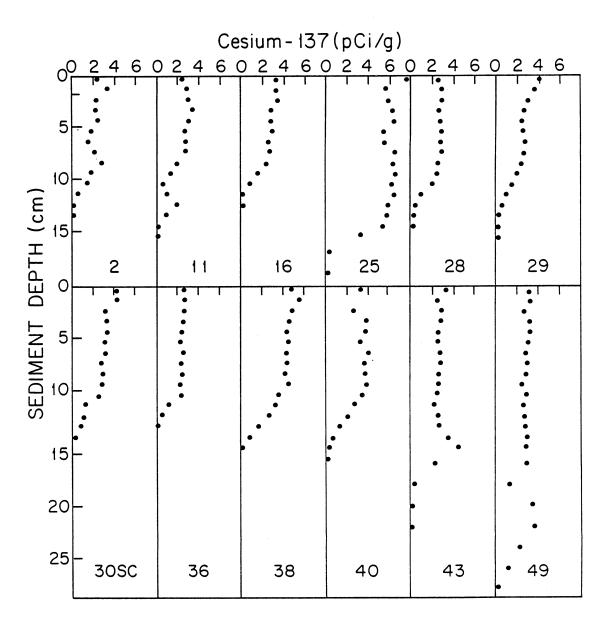
Figure 36.   Distribution of cesium-137 in selected sediment cores
(1975 data).

As part of this report, the vertical distribution of zoobenthos was determined in a number of sediment cores (Batac-Catalan et al. 1980). Previously, Robbins et al. (1977) observed that the zoobenthos occurred primarily in the zone of mixing as defined by radiocesium and radiolead profiles and that they were present in sufficient numbers to account for estimated mixing rates. A summary plot for cores examined to date from this study area, from Lake Huron and from Lake Erie, is given in Figure 37. The 90% cutoff depth is very well correlated with the depth of the mixed zone ($S = -0.2 + 1.16$ Z; $r = 0.91$, $N = 10$). Thus, there is strong circumstantial evidence that benthic organisms are primarily responsible for the mixing of near-surface sediments and the resultant alteration of radioactivity and contaminant metal profiles. Previously it had been suggested (Lerman and Lietzkie 1975) that profiles of cesium-137 as well as those of strontium-90 might be affected or even largely determined by diffusional migration. However, Robbins et al. (1977) showed that cesium-137 cannot migrate significantly in sediments by molecular diffusion as it is strongly bound to sediment solids. This result cannot be generalized to include other contaminants, tracers, or sedimentary environments however. Cesium-137 can experience significant diffusional migration in sediments which do not contain minerals with a specific affinity for this radionuclide (cf. Alberts et al. 1979). Also, a nearly conservative tracer such as Sr-90 undergoes considerable diffusion in sediments of the Great Lakes (Lerman and Lietzkie 1975).

Shown in Figure 38 is the depth of sediment mixing as determined from inspection of Cs-137 profiles. In all cases the depth of penetration of this isotope is comparable to or slightly less than the depth of penetration of contaminant metals. This result suggests that the organisms mixing sediments

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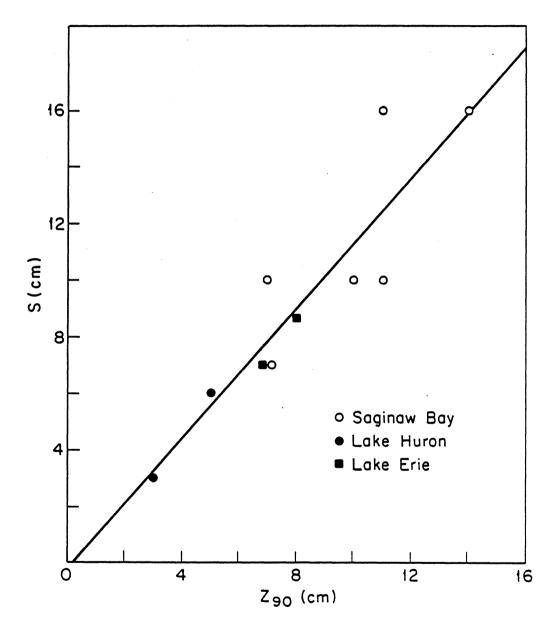
Figure 37. Relation between the depth of sediment mixing based on cesium-137 profiles and the range of zoobenthos which actively redistribute sediments (primarily oligochaetes).

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MIXED DEPTH (cm)

■ >15

▓ 10-15

░ 5-10

□ < 5

44°00'—

43°50'—

43°40' —

Bay City

⇧
N

LOWER SAGINAW BAY

0   5   10   15
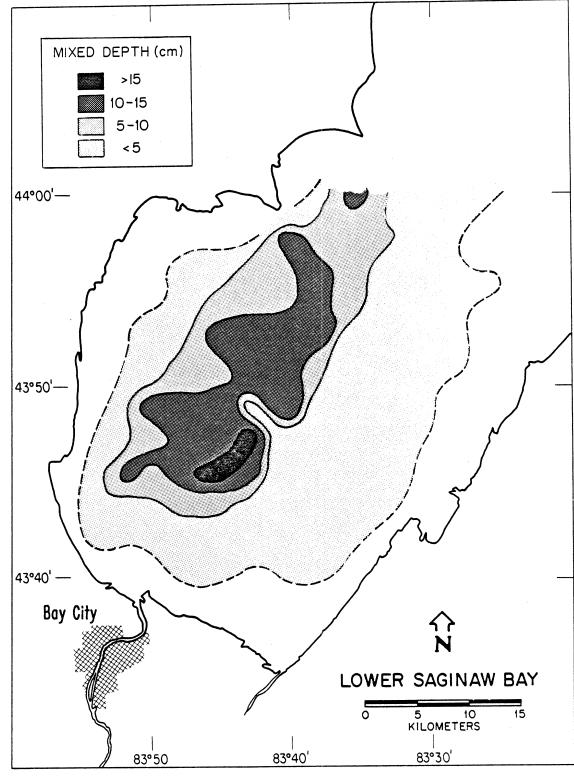KILOMETERS

83°50   83°40'   83°30'

Figure 38.   Contour plot of the depth of sediment mixing as determined
radiometrically.

were able to completely homogenize the overlay (zone 2) in the time period from about 1964 to 1975 (or about 10 years). Such inferences are based on the assumption that local contributions of Cs-137 (such as from the Saginaw River) are unimportant. Generally, loading of the isotope from watershed erosion is small. The mixed depth contours shown in Figure 38 possess features comparable to those in open lake sediments: greatest depths occur toward the centers of depositional basins. However, while mixed depths range from about 2-5 cm in the open lake basins, those in Saginaw Bay range from 5-20 cm.

The total cesium-137 stored in bay sediments is shown in Figure 39. Highest accumulations occur toward the southwestern end of the deposit and in areas of deeper water. While the pattern may be interpreted as implying a riverine source of the isotope, it must be kept in mind that the gyre-like circulation in the lower bay could easily redistribute incoming atmospheric and open-lake loadings so as to produce the observed pattern of deposition. The mean deposition within the muddy deposits was 13.9 ± 1.4 pCi/cm^2 in 1975 and 12.8 ± 2.3 pCi/cm^2 as remeasured in 1978. As very little new Cs-137 was introduced during the period from direct fallout, and if river loadings are negligible, then the expected amount stored in 1978 should be less as a result of radioactive decay. Assuming losses of Cs-137 through resuspension, the expected 1978 activity would be

$$13.9 \times e^{-0.69315 \times 3/30} = 12.96 \text{ pCi/cm}^2$$

which is close to the observed value of 12.8 pCi/cm^2.

If the loading to the lower bay were directly from the atmosphere and there were no losses via outflow or gains either from tributary inputs or from importation of the isotope from the main lake, the expected amount within the lower bay would be
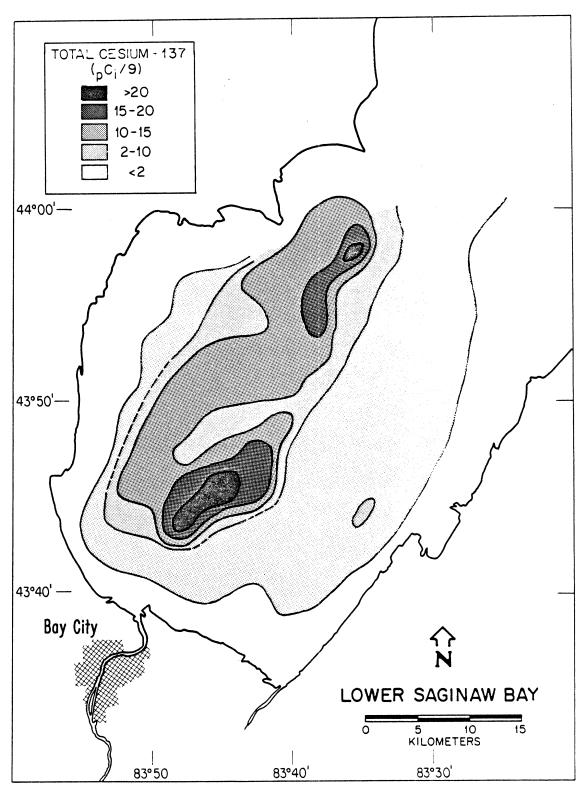
Figure 39.   Total amount of cesium-137 deposited in sediments of the
lower bay.

10 pCi/cm^2 (fallout value decay corrected to 1975) x 15.8 x 10^{12} cm^2
(area of the lower bay) = 158 Ci.

The observed inventory is

13.9 pCi/cm^2 x 3.74 x 10^{12} (area of the mud deposit) = 52 Ci.

Allowing for a maximum of 1 pCi/cm^2 deposited over non-muddy areas of the
lower bay, this amount would contribute

(15.8 − 3.74) x 10^{12} x 1.0 pCi/cm^2 = 12 Ci.

Thus, the total amount of Cs-137 in the lower bay is estimated as

52 + 12 = 64 Ci. Thus, in the absence of watershed contributions,

there is a net storage of 64/158 = 40% of the cesium-137 entering via at-

mospheric fallout. The effect of watershed inputs remains to be evaluated.

Lead-210

The lead-210 method of dating coastal marine and lacustrine sediments has

been used with increasing frequency since its first application by Krish-

naswami et al. (1971). The extensive literature concerning radioactive lead

isotopes and lead-210 in particular has been recently reviewed by Robbins

(1978). The method has been shown to be of value in dating fine-grained

sediments from all of the Great Lakes (Superior: Bruland et al. 1975, Evans

et al. 1981; Michigan: Robbins and Edgington 1975, Edgington and Robbins 1976;

Huron: Robbins et al. 1977; Erie and Ontario: Robbins et al. 1978, Farmer

1978). Generally, the method has been applied to a very limited set of cores.

Only a brief account of the lead-210 method of dating sediments is given in

this report. For a detailed discussion of the principles underlying the

method, see Robbins (1978).

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Lead-210 is produced as the indirect result of the decay of uranium
present in crustal and sedimentary materials. The principal components in the
decay scheme are:

$$U^{238} \rightarrow Ra^{226}(t_{1/2} = 1,620 \text{ yr}) \rightarrow Rn^{222}(t_{1/2} = 3.8 \text{ d})$$
$$\rightarrow Pb^{210}(t_{1/2} = 22.26 \text{ yr}) \rightarrow Po^{210}(t_{1/2} = 138 \text{ d})$$
$$\rightarrow Pb^{206}$$

Short-lived products in the decay scheme are not shown.

Some lead-210, present in sediments, is produced by in situ decay of
radium-226. Generally this is a small and nearly constant activity referred
to as supported lead-210. In addition to supported lead-210, there is an
excess which is supplied to sediments from atmospheric deposition.
Atmospheric lead-210 originates from a unique property of the uranium series
decay scheme shown above. Radium-226 decays to form the radioactive noble
gas, radon-222, which diffuses out of crustal materials into the atmosphere.
Radon-222 decays through a series of very short-lived nuclides to lead-210
which has a high affinity for atmospheric particulate matter and is rapidly
scavenged from the air. The flux of lead-210 over the Great Lakes has not yet
been measured but is expected to be around 0.5 $pCi/cm^2/yr$ and quite constant
from year to year. Once in the water, lead-210 is rapidly transferred to
sediments and this excess, not being supported by radium activity, decays
toward supported levels during burial. In sediment cores from the Great
Lakes, excess lead-210 may be roughly twenty times higher than supported
levels (cf. Robbins and Edgington 1975).

In undisturbed cores where the sedimentation rate is constant, the activity of <u>excess</u> lead-210 is given by

$$A(m) = A_o \cdot e^{-\lambda t} = A_o \, e^{-\lambda m/r} \tag{9}$$

where A_o is the excess activity at the surface (m = o), t is the time before collection (years), m is the cumulative dry weight of sediment (g/cm^2), and r is the mass sedimentation rate ($g/cm^2/yr$). The radioactive decay constant is given by $0.69315/22.26 = 0.311 \, yr^{-1}$.

The total (observed) activity is given by

$$A_{tot} = A(m) + A_f$$

where A_f is the activity of supported lead-210.

The above equations suffice to describe profiles in sediments where there is no mixing. Incorporation of the effects of rapid steady-state mixing is comparatively straight-forward for lead-210 (Robbins et al. 1977) as $A_s(t)$ in Eq. 8 is essentially constant over time. Using mass units rather than linear (cm) units and substituting A_o for $A_s(t)$ in that equation, the distribution of excess lead-210 is given by
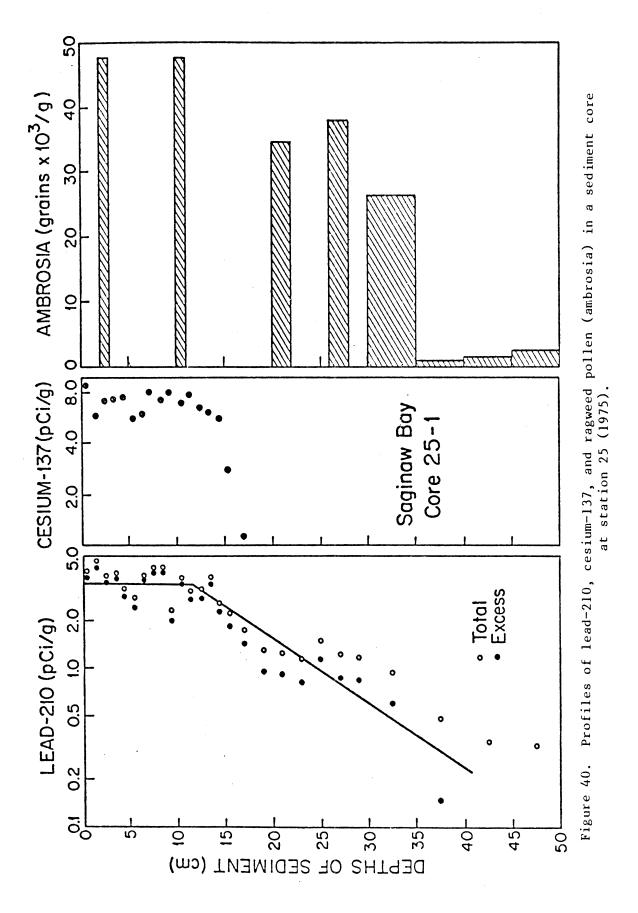
$$
\begin{array}{ll}
A_m & = A_o \, / \, (1 + \lambda s/r) \\
A(m) & = A_m \qquad m \le s \\
& = A_m e^{-\lambda \, (m-s)/r} \quad r > s.
\end{array}
\tag{10}
$$
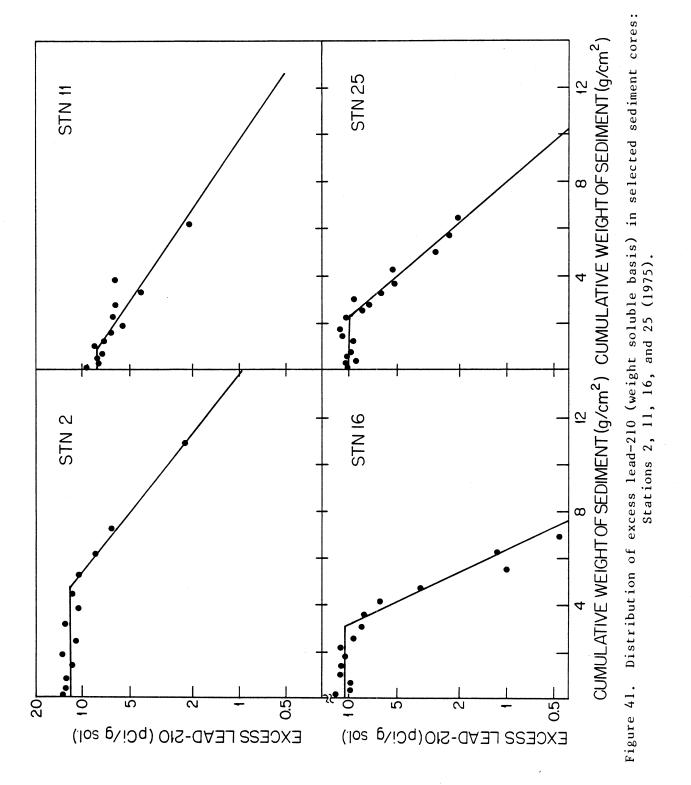
This is the equation used to obtain sedimentation rates and mixed depths from excess lead-210 profiles. Eq. 10 describes a theoretical profile in which the activity of lead-210 is constant from the sediment-water interface down to depths. Below that depth (mixed depth) the activity falls off exponentially.
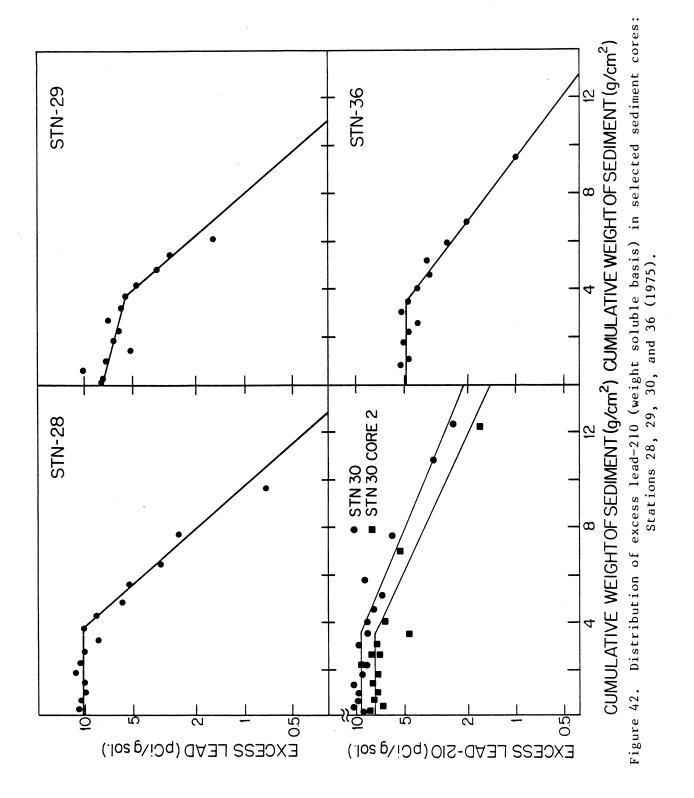
An example of the lead-210 distribution is given in Figure 40, together with the distribution of cesium-137 and ragweed (ambrosia) pollen in a core at

Figure 40. Profiles of lead-210, cesium-137, and ragweed pollen (ambrosia) in a sediment core at station 25 (1975).

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station 25 (1975). Note that over the zone of about 12 cm depth, where cesium-137 activity is essentially constant, the a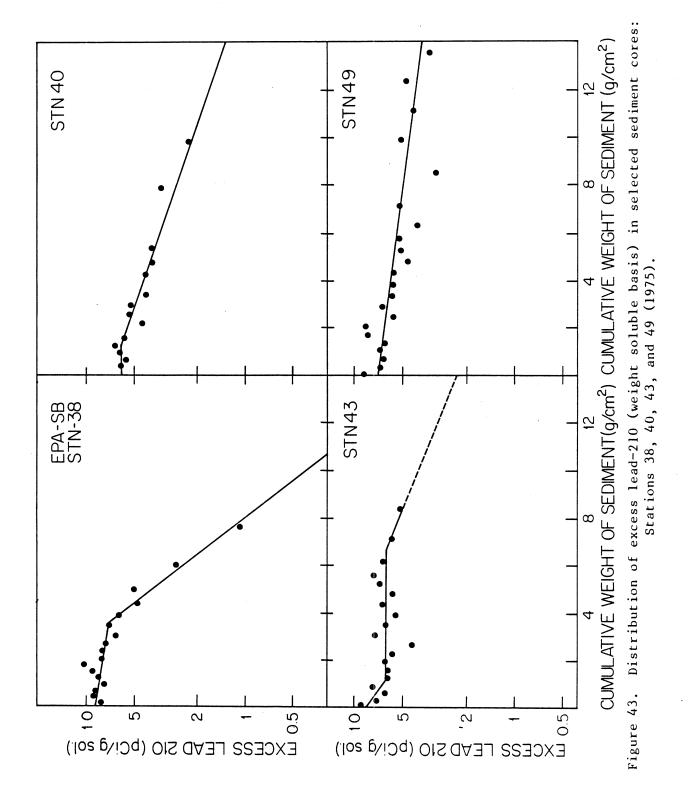ctivity of lead-210 is also essentially constant as expected if both isotopes are uniformly mixed. Below 12 cm, the activity of excess lead-210 falls off more or less exponentially, as expected, due to a combination of radioactive decay and burial. A least squares fit of model parameters to the distribution yields a mixed depth of 2.5 g/cm^2 (12 cm) and a sedimentation rate of 0.078 $g/cm^2/yr$ (0.31 cm/yr average over upper 20 cm). The ragweed distribution shown in the figure was provided by Dr. A. Kemp, formerly with Canada Centre for Inland Waters. Use of ragweed pollen data to obtain sedimentation rates in the Great Lakes is discussed in detail elsewhere (cf. Robbins et al. 1978). Following forest clearance in the Great Lakes region roughly 130 years ago, a dramatic increase in production of ragweed pollen occurred. As the grains are well preserved in recent sediments of the Great Lakes, the depth at which an increase occurs (horizon) may be used to obtain an average sedimentation rate for the past 130 years or so. In the core at station 25 the horizon is at 30-35 cm, corresponding to a cumulative sediment weight of 10.1 g/cm^2. Thus the average sedimentation rate is 10.1/130 = 0.078 $g/cm^2/yr$. Such good agreement between dating methods is completely accidental in view of the many approximations, assumptions, and uncertainties.

Distributions of excess lead-210 (on a weight soluble basis) are shown for additional cores in Figures 41-43. As can be seen, profiles exhibit the characteristic zone of mixing below which the activity decreases more or less exponentially. Summary data and model parameters derived from least squares fits are given in Table 9. These rates must be treated with some reservation because exponential portions of the profile occur at depths where there may be

Figure 41. Distribution of excess lead-210 (weight soluble basis) in selected sediment cores: Stations 2, 11, 16, and 25 (1975).

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Figure 42. Distribution of excess lead-210 (weight soluble basis) in selected sediment cores: Stations 28, 29, 30, and 36 (1975).

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Figure 43. Distribution of excess lead-210 (weight soluble basis) in selected sediment cores: Stations 38, 40, 43, and 49 (1975).

TABLE 9. Sedimentation and mixing depth data for Saginaw Bay cores.

Site No.	Supported Activity pCi/g sol	Excess Lead-210 Surface pCi/g	pCi/g sol	Mixed Depth g/cm^2	cm	Sedimentation rate g/cm^2/yr	cm/yr*	Resolution** yr
2A	0.13	2.0	13.5	5.3	10	.11	.16	48
11A	0.30	2.1	8.6	2.3?	9?	.13	.31	18
16-1	0.38	2.9	12.2	2.6	8	.043	.086	60
25-1	0.34	4.0	11.8	2.2	12	.078	.31	28
28	0.23	2.1	10.5	3.0	8	.080	.13	38
29	0.28	1.4	6.8	3.5	9	.076	.13	46
30A	0.46	3.0	10.9	4.0	11	.215	.51	19
30A-2	0.40	2.2	9.3	4.0	9	.195	.42	21
36	0.19	1.4	5.7	4.0	11	.12	.21	30
38	0.22	2.7	9.2	2.5	10	.070	.17	36
40	0.23	2.0	6.1	2.1	8	.20	.45	11
43	0.20	2.2	6.4	6	>16?	.24	.62	25
49	0.22	2.3	6.7	>10?	>22?	.67?	1.4?	15

* Average over the upper 20 cm.   ** Mixed depth (g/cm^2) / sedimentation rate (g/cm^2/gr).

gross compositional changes as evidenced by variations in major element composition and because straggling of zoobenthos into sediments below the mixed zone may produce profiles with exponential features. Trends in the apparent sedimentation rates over the mud deposit are shown in Figure 44. Highest rates occur toward the southwestern end of the deposit and decrease almost monotonically with increasing distance along the main axis of the deposit toward the far end of the lower bay. This trend could be interpreted as the effect of river loading. However, a similar trend was found earlier in sediments of the Goderich basin. Higher mass sedimentation rates occurred toward the eastern margin of the basin where enhanced deposition of dolomite occurs. Similarly, in the bay, highest apparent sediment accumulation rates tend to occur in areas of greatest concentrations of calcium and magnesium. Preferential accumulation of these silt size constituents in the southwestern end of the mud deposit may reflect prevailing current structure as much as the distribution and loading of source materials.

Also shown in Table 9 is the time resolution associated with each core. This concept has been discussed in detail elsewhere (Robbins 1980). Briefly, the effect of steady-state mixing is to smear out signals in the sedimentary record. A measure of the fidelity of the record is the time resolution with which two events may be distinguished. This time is given approximately as the residence time of a particle within the mixed layer, which in turn is given as the ratio of the mixed depth (g/cm^2) to the sedimentation rate ($g/cm^2/yr$). Within the mud deposits of the lower bay this time varies from 11 to 60 years, with a mean value for cores examined of 30 years. This latter value may be taken as the approximate mean particle integration time for these deposits.

APPARENT SEDIMENTATION
RATE (g/cm^2/yr)

44°00'—

.11

0.1

.13

.043

.078

.076

.080

0.1

.22

.070

.12

43°50'--

.20

.26

0.2

0.2

0.5

.67

0.5

43°40' —

Bay City

N

LOWER SAGINAW BAY

0   5   10   15
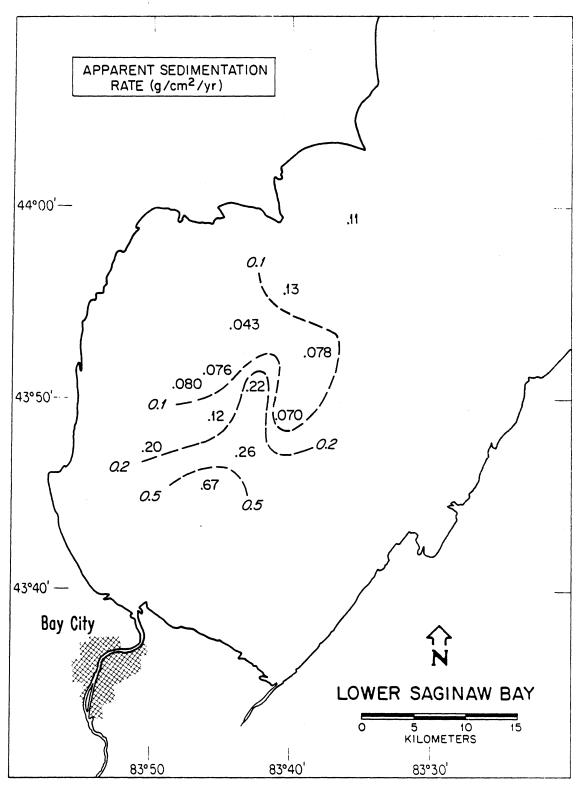KILOMETERS

83°50   83°40'   83°30'

Figure 44. Apparent sedimentation rates at selected locations in the
lower bay based on lead-210 profiles.

If resuspension of particles out of the mixed layer is an important means of exchange of contaminants between sediments and water, the effect of this integration process is twofold. At the onset of contamination loadings, rapid mixing of sediments over an interval corresponding roughly to 30 years serves to remove contaminants from the water column more efficiently. However, with the cessation of contaminant loadings, the mixed layer serves to maintain levels in the bay through resuspension with a time constant of about 30 years.

NET METAL CONTAMINANT FLUXES

In the absence of sediment mixing, the estimate of the current and historical rates of deposition of a particle bound (non-mobile) metal contaminant would be straightforward. If the concentration of a given element in the sediments corresponding to a time t in the past was $C(t)$, then the rate of deposition would be $F(t) = r*C(t)$ where r is the sedimentation rate $(g/cm^2/yr)$. The net (anthropogenic) flux would be $r*(C(t) - C_b)$ where C_b is the estimated "background" concentration.

Because of mixing, however, present and historical net fluxes cannot be estimated unless some assumption is made concerning the time dependence of the flux. Previous work (Robbins 1980, Edgington and Robbins 1976) has shown that the vertical distribution of many contaminant elements (Pb, Cu, Cd, Zn) is consistent with a roughly exponential increase in loading since 1800 and that the doubling time is approximately 20 years. Assuming that form of the loading, the rate of deposition may be inferred for the time of collection of the cores as follows:

For stable elements (with no radioactive decay), the net concentration of an element in the mixed zone is given by Eq. 8 with $\lambda = 0$ or

$$C_m(t) = \lambda e^{-\lambda t} \int_{-\infty}^{t} e^{+\lambda\tau} \, C_s(\tau) \, d\tau \qquad (11)$$

where C_s is the concentration of an element in materials deposited at the sediment surface.

In accordance with the above discussion, C_s has the form

$$C_s(t) = C_s(o) \, e^{\lambda't} \qquad (12)$$

where $\lambda' = 0.6932/t_d$ and t_d is the doubling time $\simeq 20$ years.

Substituting Eq. 11 into Eq. 12 and integrating

$$C_m(t) = \frac{\gamma}{\gamma+\lambda'} \, e^{\lambda't} \, C_s(o) \qquad (13)$$

The flux to the surface in 1975 is then

$$F_s(o) = r*C_s(o) \, e^{\lambda't} \qquad (t=0) \qquad (14)$$

$$= \frac{\gamma+\lambda'}{\gamma} \, C_m*r$$

Note then that the product C_m*r is simply the net or excess metal concentration in mixed layer times the sedimentation rate. If the time dependence of the input is essentially exponentially increasing, the correction for mixing is given as

$$F_{cor} = \frac{\gamma+\lambda}{\gamma} \qquad (15)$$

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where γ is the ratio s/r and γ^{-1} is simply the time resolution discussed above. Values of this correction factor and estimated fluxes corrected by time factors are given in Table 10. Net fluxes are consistently much higher in Saginaw Bay than in Goderich basin of Lake Huron (main depositional area) because of the much higher sedimentation rates in the bay. The total rate of accumulation of selected contaminant metals generally exceeds that expected from atmospheric loadings. Approximate atmospheric loadings are summarized by Robbins (1980). For copper, the atmospheric flux is approximately 0.41 $\mu g/cm^2/yr$ which implies a loading to the lower bay of

$$0.41 \times 15.8 \times 10^{12} \ \mu g/yr = 6.5 \text{ metric tons/yr}$$

whereas the estimated deposition is 28 metric tons/yr. Similarly for nickel, the atmospheric loading of about .23 $\mu g/cm^2/yr$ corresponds to 3.6 metric tons/yr as compared with an estimated deposition of 30 metric tons/yr. These elements would appear to have major non-atmospheric sources. In contrast, a lead atmospheric deposition of about 1.7 $\mu g/cm^2/yr$ implies a total loading of 27 metric tons per year which is very comparable to the calculated sediment deposition rate of 40 metric tons. As most anthropogenic lead in the environment results from combustion of fuel additives and coal, the atmospheric pathway is the primary route to loading of aquatic systems. Thus the agreement between these numbers supports the validity of this approach. Atmospheric loadings of zinc (2.6 $\mu g/cm^2/yr$) imply a total deposition of 40 metric tons per year as compared with 86 metric tons per year into sediments. Thus zinc is comparable to lead in terms of the predominance of atmospheric inputs into sediments of the lower bay.

TABLE 10. Model dependent net metal deposition rates in Saginaw Bay cores collected in 1975.

Site No.	γ (yr^{-1})	Fcor**	Sedimentation Rate (g/cm^{2}yr)	Net flux (μg/cm^2/yr)*					
				Cr	Cu	Ni	P	Pb	Zn
2	.021	2.7	.11	5.5	3.1	3.4	92	3.4	12.7
11	.056	1.6	.13	6.9	3.9	5.1	107	7.9	15.8
16	.017	3.1	.043	4.4	2.3	2.0	127	4.7	8.0
25	.036	2.0	.078	10.9	5.5	4.5	106	8.1	16.3
28	.026	2.3	.080	–	3.1	2.8	–	5.7	12.8
29	.022	2.6	.076	–	3.6	2.0	–	6.5	12.8
30A	.053	1.7	.215	15.0	6.2	5.5	127	8.8	20.1
36	.033	2.0	.12	5.0	6.2	6.2	–	6.0	13.2
38	.028	2.2	.070	6.9	4.8	4.9	–	8.3	15.7
40	.091	1.4	.20	22.4	10.9	9.5	–	14.0	27.7
43	.023	2.5	.24	21.0	15.0	10.8	–	22.8	48.0
49	.067	1.5	.67	46.2	24.1	40.2	–	32.2	73.4
Mean (SB)		2.1	0.17	14.4	7.4	8.1	111	10.7	23.0
Mean (SLH, Goderich Basin)		2	0.035	0	0.58	1.1	0	2.4	3.1
Total Accumulation Rates in Saginaw Bay (1975) (metric tons/year)			6.3×10^5	54	28	30	420	40	86

*Based on acid soluble concentrations.

**$F_{cor} = (\gamma + \lambda')/\gamma$ $\lambda' = 0.6932/20$ (yr^{-1})

VERTICAL DISTRIBUTION OF DISSOLVED SILICON AND PHOSPHORUS

The vertical distribution data are available for dissolved Ba, Ca, Fe, Mg, Mn, P(SRP), K, Na, Si(SRS), and Sr (Table 31 of the Data File, see page 96) for two cores from Saginaw Bay (station 30) and from Lake Huron sites as well. Results for the Saginaw Bay cores are generally comparable to those from the open lake (in terms of pore water concentrations, gradients, and fluxes). For a detailed discussion see Robbins (1980). Of particular interest are the distribution of SRP and SRS. Soluble reactive phosphorus concentrations in overlying water are essentially undetectable (<0.1 ppm). In pore water, concentrations rise to a maximum of 5.5 ppm at 4-5 cm depth, decreasing with increasing sediment depth to values of around 3 ppm. Values in a replicate core are somewhat sporadic because of minor oxygen contamination (see Robbins 1980). The gradient at the sediment water interface is about 1.5 μg PO_4/cm^4. Gradients of PO_4 in the open water sediments were 0.5-0.8 μg PO_4/cm^4. Assuming an effective diffusion coefficient of about 5 x 10^{-6} cm^2/sec or 160 cm^2/yr, the apparent flux across the sediment surface is about 240 μg/cm^2/yr. The net downward flux of acid soluble P (as PO_4) is 1,680 μg/g x 0.2 g/cm^2/yr = 330 μg/cm^2/yr. Within the uncertainties of the calculation these fluxes are comparable, suggesting steady-state conditions with respect to incoming and outgoing fluxes of SRP. For silicon, the concentration in overlying water is about 2 μg/ml. The distribution in core 30A and 30A2 is shown in Figure 45. The break in concentration values around 5 cm is unexplained but reproducible in two cores. Equilibrium concentrations are around 25 μg Si/ml. The gradient at the sediment water interface is about 5.5 μg/cm^4 which implies a flux of 660 μg/cm^2/yr, assuming a diffusion coefficient of 120 cm^2/yr (See Robbins 1980). This estimated flux is at the low end of the range of fluxes
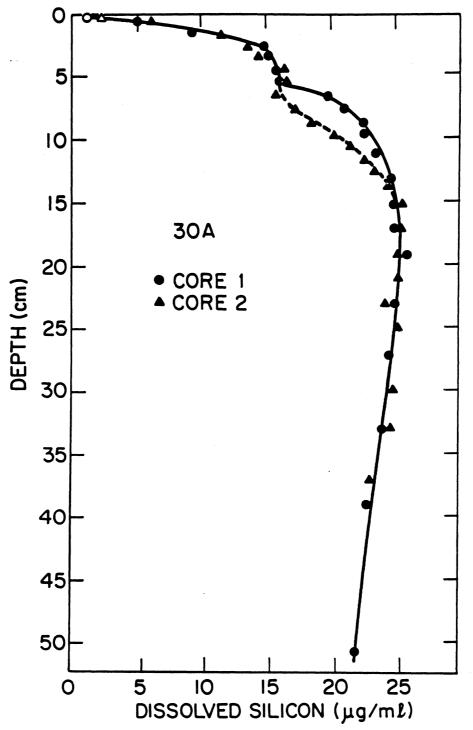
SAGINAW BAY CORES
(EPA-SLH-75)

Figure 45. Vertical distribution of soluble reactive silicon (SRS) in two cores from station 30.

calculated from pore water gradients in southern Lake Huron cores (Robbins 1980), 750-1,700 μg Si/cm^2/yr, and as measured directly in northern Lake Huron cores by Remmert et al. (1977), 1,020-2,050 μg Si/cm^2/yr.

NUTRIENT FLUXES

The results of direct flux measurements for silicon are shown as a function of season in Figure 46 for cores taken at station 31. Fluxes measured directly in cores are consistently higher than values based on pore water gradients and show a marked seasonal variation with maximum silicon release occurring during August. The seasonal variations in this flux may be attributed primarily to sediment temperature variations as illustrated by Figure 47. The solid line represents the conventional thermodynamic description (Arrhenius equation) of the temperature dependence of dissolution with an activation energy of 16.3 k/Cal/mole as determined by least squares methods.

The role of organisms (especially chironomids) in silica regeneration is well documented for other lakes (Tessenow 1964) and may be expected to occur in Saginaw Bay where such organisms occur. The silica fluxes measured in a series of cores during fall cruises when chironomids were present are provided in Table 11. It can be seen that the dominant benthic taxon in terms of numbers are the immature tubificid worms. However, densities of these organisms correlate poorly with the silicon flux, as can be seen from Table 12. Because of the limited number of observations, most correlations are not significant. However, the correlation between the Si flux and the density of chironomids is high and significant for both observation periods (Fig. 48). In this experiment, other nutrients were measured as well and
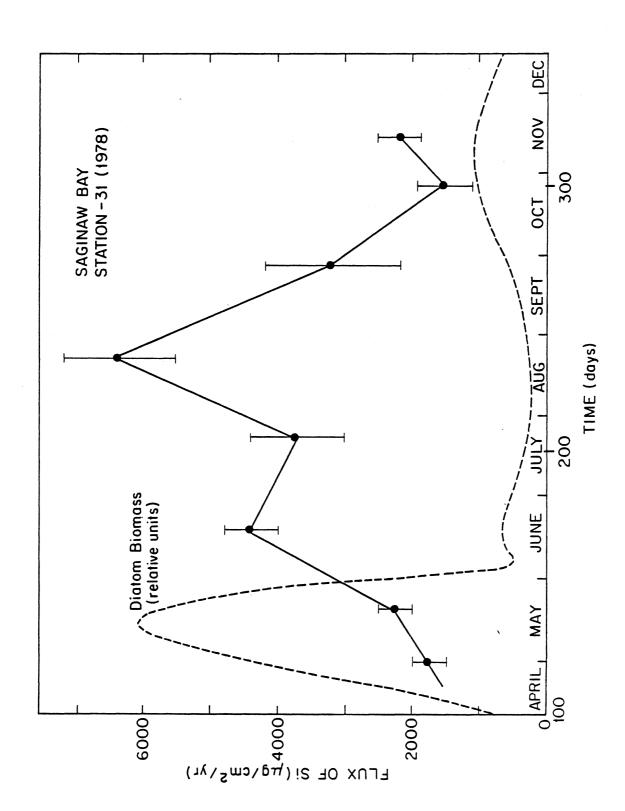
85

Figure 46. Seasonal variations in the flux of soluble reactive silicon from sediments at station 31.
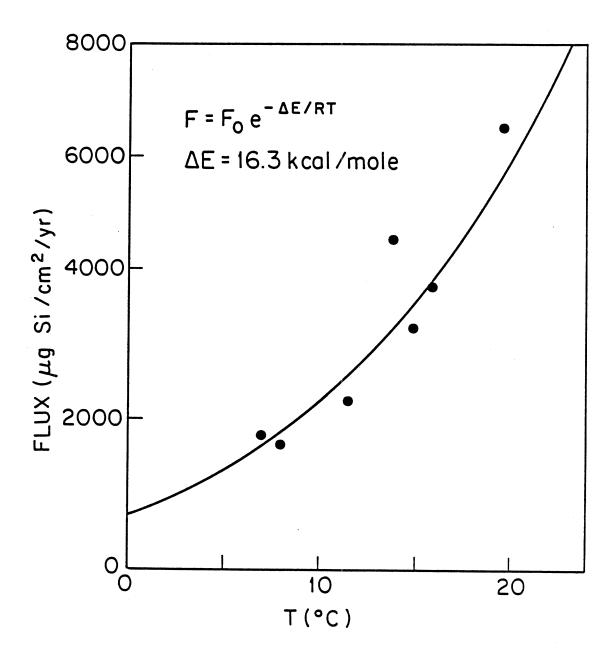
Figure 47. Temperature dependence of the soluble reactive silicon flux at station 31.

TABLE 11. Zoobenthos density and soluble reactive silicon fluxes from cores collected in Saginaw Bay, Lake Huron.

| Cruise Number | Core | Density (number/m^{-2}) | | | | Silicon Flux (μg/cm^2/yr) |
| | | Tubificidae | | Naididae | Chironomidae | |
		Mature	Immature			
7*	1	850	40,000	5,900	0	1,100
	3	850	65,000	7,900	0	770
	1'	280	8,200	850	560	1,800
	2'	1,700	29,000	8,200	850	2,700
	3'	2,300	18,000	560	560	1,680
8**	1	1,400	23,000	0	1,130	3,600
	2	280	5,600	0	0	1,300
	8	280	5,600	0	280	1,600
	2'	280	29,000	13,000	560	2,400

* October, 1978. **November, 1978.

TABLE 12. Correlations* between nutrient fluxes and benthic organism densities in cores from station 31 in Saginaw Bay, Lake Huron.

(CRUISE 7)

Organism Group	Phosphate (PO$_4$)	Ammonia (NH$_3$)	Nitrate (NO$_3$)	Sulfate (SO$_4$)	Silicon (Si)
Tub. Mature	0.93	−0.09	−0.17	−0.75	−0.07
Immature	0.07	−0.82	0.69	−0.54	−0.36
Naididae	−0.19	−0.49	0.13	−0.41	−0.29
Chironomidae	0.11	0.74	0.04	0.04	0.97
Total	0.06	−0.69	0.55	−0.56	−0.26

(CRUISE 8)

Organism Group	Phosphate (PO$_4$)	Ammonia (NH$_3$)	Nitrate (NO$_3$)	Sulfate (SO$_4$)	Silicon (Si)
Tub. Mature	0.41	0.92	0.23	0.97	0.88
Immature	0.23	0.14	0.93	0.22	0.49
Naididae	−0.30	0.63	0.78	−0.50	0.13
Chironomidae	0.09	0.63	0.25	0.76	0.99
Total	−0.9	−0.05	0.94	0.01	0.62

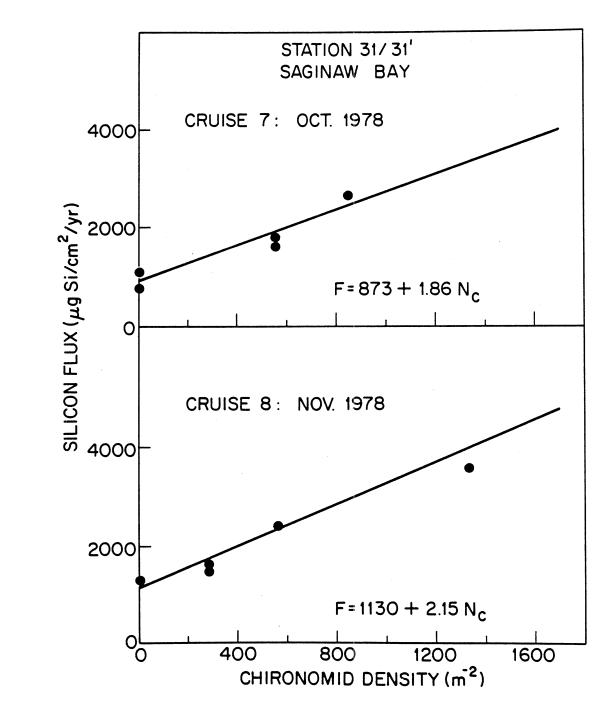*Correlations which are significant on both sampling periods are underlined.

Figure 48. Relation between the SRS flux at station 31 and density
of Chironomid larvae during the fall months (1978).

correlations which are persistently higher over both cruises are underlined in Table 12.

The results for silicon suggest the relationship:

Flux = 1,000 + 2 x chironomid larvae density,

where the flux is in micrograms $Si/cm^2/yr$ and the density is in numbers m^{-2}. As the mean density of chironomid larvae at this location is about 500 m^{-2}, roughly half the flux of silicon from the sediments is attributable to the presence of these organisms. This circumstantial evidence for the effect of chironomids is strengthened by considering Tessenow's experiments with sediments from Lake Heiden, Germany (Tessenow 1964), in which he demonstrated a causal relationship. Addition of chironomids (Plumosus group) to his sediments resulted in enhanced silicon release. Converting Tessenow's results to the above form, his experiments yield:

Flux = 1,000 + 4 x chironomid larvae density.

Graneli (1977) has also observed that Chironomus plumosus larvae increase the release of silica as well as phosphorus from sediments of several lakes in Sweden. It would therefore seem likely that, at least in shallow waters of the Great Lakes where fine-grained sediments can be found, such as lower Saginaw Bay and most of Lake Erie, chironomid larvae may play a major role in the regeneration of silicon from sediments. In Lake Erie, average chironomid densities may be as high as 1,000 m^{-2} (P. McCall, Dept. of Geological Sciences, Case Western Reserve University, Cleveland, Ohio, pers. comm.). That these organisms may enhance silicon fluxes does not necessarily mean that their removal or exposure to aquatic pollutants will result in a long-term reduction in the capacity of the sediments to return silicon to overlying waters. It is always possible that the ecological niche represented by

processing of silica-rich diatom detritus can be filled by another biotic or abiotic component. It should be noted that Robbins and Edgington (1979) found that the flux of Si from sediments in Lake Erie is proportional to the concentration of amorphous silicon in surface sediments. This result suggests that the flux is dominated by dissolution of particulate silica recently deposited on the sediment surface. Processing of such materials by chironomids, which can selectively attract and ingest diatom fragments by controlling water movements in the vicinity of their burrows, (D. White, School of Natural Resources, University of Michigan, Ann Arbor, Michigan, pers. comm.), would enhance silica fluxes but reduce pore water silica gradients.

CONCLUSIONS

During the period from 1975 through 1978, sediment cores and grab samples were collected from over 100 sites evenly arrayed in lower Saginaw Bay. This intensive coverage of the lower bay, with subsequent comprehensive analysis of sediments for over 30 elements, as well as other properties, has provided a detailed picture of the type of sedimentary materials present and patterns of major element and metal contaminant concentrations. This study has revealed an extensive mud deposit in the lower bay covering about 400 km^2, oriented predominantly with the bathymetric contours but skewed toward the western side of the bay in shallower regions, presumably as a result of prevailing gyre-like current patterns. The clay content of this deposit exceeds 50% toward the center and in parts lying in deeper water. The mean grain size in the high clay areas exceeds 6 phi units. Grain sizes increase toward the margins of this basin, exhibiting the classic pattern associated

with hydrodynamic particle sorting. Calcium family elements (Ca, Mg, and inorganic carbon) are preferentially concentrated at the southwestern end of the deposit, either because of the distribution of source materials or current structure in the bay.

Iron and organic carbon exhibit highest concentrations in the clay-rich sediments. Most contaminant metals such as lead, zinc, copper, nickel, and chromium are strongly correlated with iron concentrations ($r > 0.9$ in most cases for $N > 30$) and thus have very similar surface concentration patterns. Concentrations of contaminant metals in surface sediments are consistently lower than concentrations in depositional basins of the open lake. Because the Saginaw River is considered to be a strong tributary source of contaminants, low metal concentrations in lower bay sediments require explanation. At least two processes reduce concentrations: (1) dilution of contaminants by a greater amount of allochthonous material in the bay, and (2) intensive reworking of sediments by zoobenthos. Corrections made for dilution effects show that chromium is significantly higher in sediments of Saginaw Bay than in open lake deposits. Vertical distributions of minor elements, cesium-137 and lead-210, show that the upper 10-25 cm of sediment are extensively reworked. The depth of sediment mixing varies systematically over the deposit, with highest values occurring toward the centers in fine-grained materials.

Vertical distributions of benthic organisms (primarily worms) indicate that 90% of the zoobenthos occur within the zone of mixing as determined radiometrically. Thus, organisms are probably responsible for sediment mixing. Numbers of benthos range from 10,000 to 50,000 m^{-2} and are sufficiently abundant to recycle particle bound contaminants in the mixed zone annually.

The total amount of cesium-137 stored in sediments of the lower bay is estimated to be 64 Ci, as compared with an estimated 158 Ci deposited over the same area from cumulative atmospheric fallout (decay corrected to 1975). In the absence of tributary contributions, the muddy deposit appears to be about 40% efficient in retaining this radionuclide. Integrated amounts of contaminant metals such as Cr, Cu, Ni, Pb, and Zn ($\mu g/cm^2$) far exceed amounts stored in offshore deposits. A comparison with atmospheric loadings shows that Cr, Cu, and Ni especially have strong non-atmospheric sources in the bay. Thus, relatively low surface concentrations of these elements conceal the fact that much contamination has been reworked downward to appreciable depths. Total inventories of metal contaminants in metric tons are: Cr, 1,100; Cu, 590; Ni, 590; P, 11,000; Pb, 850; and Zn, 1,800.

Sediment mixing is, in fact, so deep that cesium-137 provides little or no information on sedimentation rates. However, lead-210 appears to give valid rates. Sedimentation rates based on ragweed pollen data and lead-210 in one core are very consistent. Values determined from lead-210 in 12 cores range from 0.07 to 0.24 $g/cm^2/yr$ and imply a total mass accumulation in the deposit of 6.3×10^5 metric tons per year. The relatively few sedimentation rate values indicate a systematic variation in rate over the deposit, with highest rates occurring at the southwestern end in proximity to the Saginaw River. Contaminant metal current deposition rates are estimated using a model of steady state mixing and exponential increase in loading with a 20 year doubling time. Annual loadings are estimated in metric tons/year as: Cr, 54; Cu, 28; Ni, 30; P, 420; Pb, 40; and Zn, 86.

In combination with sediment mixing depths, sedimentation rates provide a measure of the particle residence time in the mixed layer. This time is also

equivalent to the time resolution in cores and, to the extent that resuspension of particle-bound contaminants from the mixed layer controls concentrations in the water column, is also the response time for recovery of the bay as a closed system to cessation of external contaminant loads. In the cores examined, this time varies from 11 to 60 years with a mean of 30 years. This latter value is presently the best estimate of mixed layer residence time to be used in bay-wide eutrophication models involving resuspension processes.

Direct flux measurements provided the following average values over the period from April 1978 to November 1978: P, -530 μg P/cm^2/yr; N(NH$_3$), +200 μg N/cm^2/yr; N(NO$_3$), -360 μg N/cm^2/yr; and Si, 3,000 μg Si/cm^2/yr. Releases of Si constitute a major input of Si to the bay. The flux of silicon from sediments exhibits an annual cycle ranging from about 1,500 μg/cm^2/yr in the spring to a maximum of about 6,000 μg/cm^2/yr in August. The mean flux may be reliably predicted from thermodynamic expressions and the sediment temperature. During the fall months the flux in individual cores is strongly correlated with the numbers of chironomid larvae present. Correlations between other nutrient fluxes and organism densities are generally insignificant.

Further studies attempting to account for the behavior of contaminants and materials in the lower bay system must take account of zoobenthos-mediated integration processes occurring in sediments. A further deception occurring as a result of dilution of contaminants by inert materials and extensive reworking should be considered: low concentrations of contaminants in bulk sediment do not necessarily imply reduced transfer up the food chain by benthos. Their particle selective feeding behavior may allow them to take full advantage of contaminants on food particles distributed throughout the reworked zone. Experience with intensive coring in the lower bay as well as

the open lake demonstrates the high degree of spatial heterogeneity in sediment composition and accumulation/mixing rates within depositional basins. Sediment budget calculations, if they are to be realistic, must take account of sediment variability. In modelling the behavior of contaminants and nutrients in the water column, depositional and non-depositional zones should be treated separately with realistic model elements characterizing integration and resuspension processes. Direct flux measurements are to be preferred to pore water gradient flux estimates because of a multiplicity of effects, including surface dissolution processes and zoobenthos mediated exchange of solutes.

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DATA FILE

The complete set of data on which this report is based includes grain
size distributions, elemental concentrations in sediments and in pore water,
nutrient fluxes, abundances of zoobenthos and element regression tables.
The 278-page data file is available from the author upon request (J. A.
Robbins, Great Lakes Environmental Research Laboratory, 2300 Washtenaw Ave.,
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